SANDIA REPORT
SAND2001-8524
Unlimited Release
Printed October 2001

BAC-G2 Predictions of Thermochemistry for Gas-Phase Aluminum Compounds

Mark Allendorf, Carl Melius, Biljana Cosic, Arthur Fontijn

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/ordering.htm

BAC-G2 Predictions of Thermochemistry for Gas-Phase Aluminum Compounds

A manuscript submitted to *Journal of Physical Chemistry A*
September, 2001

Mark D. Allendorf
Sandia National Laboratories
Combustion Research Facility
Livermore, CA 94551-0969

Carl F. Melius
Lawrence Livermore National Laboratory
Livermore, CA 94551

Biljana Cosic
Arthur Fontijn
Dept. of Chemical Engineering
Rensselaer Polytechnic Institute
Troy, NY 12180-3590

Abstract

A self-consistent set of thermochemical data for 55 molecules in the Al-H-C-O-F-Cl system are obtained from *ab initio* quantum-chemistry calculations using the BAC-G2 method. Calculations were performed for both stable and radical species. Good agreement is found between the calculations and experimental heats of formation in most cases where data are available for comparison. Electronic energies, molecular geometries, moments of inertia, and vibrational frequencies are provided in the Supporting Information, as are polynomial fits of the thermodynamic data (heat of formation, entropy, and heat capacity) over the 300—3000 K temperature range.

(This page intentionally left blank)

I. Introduction

Chemical vapor deposition (CVD) of aluminum and aluminum compounds is of interest for a variety of technologies. For example, formation of conduction lines in the fabrication of microelectronic devices is a well-established technology. CVD processes are also being developed to produce thermal barrier coatings, alumina -based ceramics, and hard coatings for abrasion and corrosion resistance. The formation of volatile aluminum compounds is also a key element in plasma etching processes. Accurate thermochemical data (± 2 kcal mol^{-1} or better) for gas-phase species, in the form of heats of formation, heat capacities, and entropies, are an essential element in the development of computational models used to simulate CVD processes. Unfortunately, such data are often not available, particularly when organic ligands are involved. Group-III compounds (i.e., those containing B, Al, Ga, In, or Tl) are typical in this regard, in that reliable thermochemistry is generally available in standard compilations[1-4] for only the closed-shell halides.

Theoretical methods can be of great value in filling the many gaps that exist in thermochemical data bases.[5] Among the many *ab initio* techniques that have been developed during the last fifteen years is G2,[6,7] a composite method that combines a series of calculations with empirical corrections to simulate a higher level of theory. This method has been used successfully to predict heats of formation for compounds in the first and second row; for a standard test set of 148 molecules, the average deviation from experiment is ±1.58 kcal mol^{-1}, with a maximum deviation of 8.2 kcal mol^{-1}.[7] Accuracies at this level are necessary for such data to be useful for CVD model development. The accuracy of the G2 method for many classes of compounds relevant to CVD has not been established, however. For example, we are unaware of any application of G2 to Group-III organometallic compounds, whose use as CVD precursors is common, because films can be deposited at lower temperatures than are typically required when halogenated precursors are used.

We recently developed a modification of the G2 method known as BAC-G2[8] (bond-additivity corrected-G2) that incorporates additional empirical corrections that further improve the accuracy of G2. While such improvements are in many cases unnecessary for small molecules, such as those included in the standard G2 test set,[7] they become increasingly important in larger molecules where the accumulation of errors can decrease the accuracy of thermodynamic predictions significantly. These corrections also yield more accurate heats of formation for an important class of CVD precursors, halide compounds, for which the G2 method performs poorly.[9,10] In this paper, we report BAC-G2 predictions of heats of formation and bond energies for compounds containing aluminum. The literature contains several reports of thermodynamic data for aluminum-containing species using theoretical methods, including a recent investigation using the G2 method by Swihart and Catoire.[11] Our investigation focuses on the thermochemistry of monomeric aluminum compounds containing bonds to H, CH_3, OH, F, and Cl and includes many species not treated in earlier work. In addition to reporting the heats of formation for 55 molecules, we discuss bond energies for many of the compounds examined and trends exhibited by the various homologous series within the set. This work expands and completes two preliminary investigations published earlier by us.[12,13]

II. Theoretical Methods

A. Overview of the BAC-G2 Method. The BAC-G2 method applies the BAC corrections to the standard G2 method,[6] using Gaussian-94.[14] The electronic-structure calculations to determine the geometry, vibrational frequencies, and electronic energies are the same as those in the G2 method. Specifically, the geometry and vibrational frequencies in the BAC-G2 method are obtained from a Hartree-Fock (HF) calculation (restricted Hartree-Fock, RHF, for closed shell molecules and unrestricted Hartree-Fock, UHF, for open shell molecules) using the 6-31G(d) split-valence basis set with polarization functions on the heavy atoms. At this level of theory, vibrational frequencies are systematically too large compared to experimental values. We therefore scale the HF harmonic frequencies downward by 12 per cent. The electronic energies at the QCI, MP4, and MP2 levels of theory, as well as the collective G1, G2MP2, and G2 electronic energies, are taken directly from the output of the G2 method. The basis sets are the same as those defined in the standard G2 method. The geometry used in the single-point calculations is obtained by reoptimizing the HF geometry at the MP2 level, again as defined in the G2 method.

The BAC corrections for the BAC-G2 method are those defined previously.[8] Briefly, three types of corrections (E_{BAC-}; units of energy) are used: atomic, molecular, and bondwise, indicated in Equations (1)—(4) below. The atomic correction depends on the atom type:

$$E_{BAC\text{-}atom} = \sum_{k} E_{BAC\text{-}atom}(A_k) \qquad (1)$$

where the sum runs over all the atoms in the molecule. The value of $E_{BAC\text{-}atom}(A_k)$ depends on the atom type and A_k is an adjustable parameter.

The molecular BAC correction arises from errors in the overall electronic structure of the molecule. The BAC correction for this term is given by

$$E_{BAC\text{-}molecule} = E_{BAC\text{-}elec\ pair} \qquad (2)$$

where $E_{BAC\text{-}elec\ pair}$ depends on the difference between the spin of the molecule and the sum of the spins of the constituent atoms:

$$E_{BAC\text{-}elec\ pair} = K_{Elec\ pair}\left(Spin_{Molecule} - \sum_{atom} Spin_{Atom}\right). \qquad (3)$$

where $K_{Elec\ pair}$ is an empirically adjusted parameter for a given BAC method and "Spin" refers to the S quantum number.

The third type of BAC correction depends on the formation of chemical bonds. In this instance, we distinguish between bonds and pair-wise interactions. A bond is taken to mean the formation of an electron pair between the atoms. This correction addresses systematic errors arising from electron-pairing not covered by Eqn. 3. The correction for each bond A-B in the molecule having neighbors C and D (e.g., C-A-B-D) is given by

$$E_{BAC\text{-}bond}(AB) = A_{AB}\, e^{-\alpha R_{AB}} + \sum_{C} B_{CA} + \sum_{D} B_{DB}, \qquad (4)$$

where the first term is the correction for the bond alone, while the corrections for its nearest neighbors are treated as a sum of corrections for each neighbor of the form

$$B_{CA} = B_C + B_A. \qquad (5)$$

The B_A's are constants that depend only on the type of atom. The bond-distance dependence in Eqn. 4 exists only in the first term for the bond itself. Furthermore, α no longer depends on the type of bond, as it did in the original BAC method.[15] Note that the bond-wise corrections do not go to zero at infinity, due to the terms $\sum B_{CA} + \sum B_{DB}$ defined by Eqn. 4.

The parameters for each of the corrections are given in Table I; values of all parameters with the exception of those for aluminum (see below) were determined previously.[8] The atomic corrections (Eqn. 1) are straightforward. For the bond-wise corrections (Eqn. 4), the α exponent is taken to be 3.0 $Å^{-1}$, while the pre-exponential coefficient A_{AB} is taken to be the geometric mean of the individual atom types, i.e.,

$$A_{AB} = -(A_{AA}\, A_{BB})^{1/2}. \qquad (6)$$

Equation 4 also includes contributions from the nearest-neighbor B_{ij} terms (defined by Equation 5). The accuracy of the parameters comprising these terms (see Table I) is difficult to assess because of their small size. This is due to the fact that to date we have only applied the BAC-G2 method to relatively small molecules (less than seven heavy, i.e., non-hydrogen, atoms), for which accurate experimental thermodynamic data exist. However, these terms become quite significant for larger molecules and for halides (see below). Unfortunately, given the limited

Table 1. BAC-G2 Parameters (Energies in kcal-mol^{-1})

$K_{Elec\ pair}$ = 0.860			
Atom	A_{Atom}	B_{Atom}	A_{ii}
H	0.485	-0.146	1.462
C	1.081	0.051	0.0
N	1.498	-0.010	2.281
O	-0.501	-0.010	114.3
F	-1.942	0.215	373.1
Al	-1.500	0.000	300.0
Cl	-0.776	0.087	1433.7

accuracy of experimental data for larger non-hydrocarbon, unsaturated gas-phase species it will remain difficult to establish the accuracy of the B_{atom} terms.

The corrected heat of formation at 0 K (ΔH_{f0}^{o}) can now be obtained from the calculated electronic energy. First, the electronic energy is added to the zero-point energy (which is automatically included in the G2(0 K) output of the Gaussian-94 code). Next, the resulting energy is subtracted from the electronic energies of the atoms to give an electronic heat of atomization:

$$E_{\text{atomization}} = \sum_{i}^{n} E_i(\text{atoms}) - (E_{ab\ initio}\,(\text{molecule}) + E_{\text{ZPE}}) \tag{7}$$

Referencing this energy against the experimental ΔH_{f0}^{o} at 0 K of the atoms (given in Table 3) in the gas phase yields the uncorrected ΔH_{f0}^{o} :

$$\Delta H^{\circ}_{\text{f0, uncorrected}} = \sum_{\text{atoms}} \Delta H^{\circ}_{f0,\text{atoms}} - E_{\text{atomization}} \tag{8}$$

Subtracting the BAC corrections from this energy finally yields ΔH_{f0}^{o} at 0 K:

$$\Delta H^{\circ}_{\text{f0,BAC}} = \Delta H^{\circ}_{\text{f0,uncorrected}} - E_{\text{BAC-Correction}} \tag{9}$$

Heats of formation, entropies, and free energies at various temperatures are then obtained using equations derived from statistical mechanics (the same procedure as in the original BAC-MP4 method).[15,16] Thus, for finite temperatures, the raw G2 energies (without BAC corrections) obtained from the BAC-G2 method do not correspond to those from the output of a Gaussian G2 calculation, since hindered rotors are included in the BAC procedure.

Using an *ad hoc* expression similar to that formulated for the earlier BAC-MP4 method[15,16] we obtain an estimate of the error (or confidence level) in the BAC-G2 method. In this case, we

use the similarities between the G1 and G2-MP2 methods and the G2 method itself as an indication of the error:

$$\text{Error (BAC-G2)} = \text{Sqrt } \{ 1.0 \text{ kcal-mol}^{-1} + (\Delta H_{BAC\text{-}G2} - \Delta H_{BAC\text{-}G2MP2})^2 + (\Delta H_{BAC\text{-}G2} - \Delta H_{BAC\text{-}G1})^2 \}. \quad (10)$$

B. Determination of BAC parameters for aluminum. The BAC parameters for aluminum were determined by optimizing the heats of formation predicted by BAC-G2 for a set of aluminum compounds whose heats of formation are considered well known. The compounds used are the trivalent species AlH_3, AlF_3, and $AlCl_3$, the diatomics AlH, AlF, and AlCl, as well as the constituent atoms. The parameters in Table I represent a compromise that yields the best overall accuracy (predicted heats of formation within ± 2 kcal mol^{-1} of accepted experimental values) for these species.

Note that, in contrast to the original BAC-MP4 method,[15,16] in which the heat of formation for isolated atoms was set to the experimental value, the atomic heats of formation obtained from the BAC-G2 method differ somewhat from the experimental values. For example, the BAC-G2heat of formation for Al(g) is 80.144 kcal mol^{-1} at 298 K, while Gurvich et al. report 78.87 ± 0.71 kcal mol^{-1}.[2] This difference results from the fact that the objective of the BAC-G2 method is to obtain accurate heats of formation for molecular species, which are the data most often needed for practical problems. Thus, some of the systematic error in the G2 calculation is shifted into the predictions for the atoms in order to obtain better agreement with well-established molecular heats of formation.

III. Results

A. Heats of formation and bond dissociation energies. Results of applying the BAC-G2 method to species in the Al-H-C-O-F-Cl system are presented in Tables 2—6, which list the atomic (Equation 1), molecular (Equation 2), and bond-wise (Equation 4) corrections for all molecules examined (Table 2); heats of formation at 0 K ($\Delta H_f°(0\text{ K})$) at various levels of theory, as well as the atomization energy at the BAC-G2 level (ΣD_0; Table 3); $\Delta H_f°(298\text{ K})$ and references to values from experiments and theory in the literature (Table 4); thermodynamic parameters at various temperatures (Table 5); and selected bond dissociation energies at 298 K (Table 6). In the Supporting Information (Tables S7 – S11), we also provide raw electronic energies at the G2 level, atomic coordinates, vibrational frequencies, moments of inertia, and polynomial fits of the thermodynamic data suitable for use with the CHEMKIN software.[17] As has been typical in previous publications involving the BAC-MP4 series, [15,16,18-25] we focus our discussion on the predicted thermochemical parameters, rather than on the ab initio calucations themselves.

Table 2: Bond Additivity Corrections for the G2 Level of Theory (kcal mol^{-1}). Bond lengths in Å. Number of bonds given in parenthesis.

Species	Al-H bond length	BAC	Al-Cl bond length	BAC	Al-C bond length	BAC	Al-O bond length	BAC	Al-F bond length	BAC	C-H bond length	BAC	Cl-H bond length	BAC	C-O bond length	BAC	O-H bond length	BAC	Atomic[a]	Molecular[b]
AlH_3	1.589 (3)	-0.11																	-0.05	-1.72
AlH_2	1.600 (2)	0.03																	-0.53	-0.86
AlH	1.659	0.14																	-1.02	-0.86
$AlCl_3$			2.069 (3)	1.49															-3.83	-1.72
$AlCl_2$ $^2A_1$			2.097 (2)	1.30															-3.05	-0.86
AlCl $^1\Sigma$			2.135	1.08															-2.28	-0.86
AlF_3									1.645 (3)	2.84									-7.33	-1.72
AlF_2 $^2A'$									1.659 (2)	2.52									-5.38	-0.86
AlF $^1\Sigma$									1.671	2.23									-3.44	-0.86
$Al(OH)_3$, C_3 axis							1.712 (3)	0.91									0.967 (3)	0.70	-1.55	-4.30
$Al(OH)_2$ $^2A_1$ planar, trans, trans							1.721 (2)	0.90									0.968 (2)	0.70	-1.53	-2.58
AlOH $^1A'$ linear							1.689	1.01									0.959	0.72	-1.52	-1.72
$Al(CH_3)_3$					1.969 (3)	-0.18					1.096 (6)	-0.14							6.11	-6.88
											1.094 (3)	-0.14								
$Al(CH_3)_2$ $^2A'$					1.978 (2)	-0.23					1.096 (4)	-0.14							3.57	-4.30
											1.092 (2)	-0.14								
$AlCH_3$ $^1A_1$					1.994	-0.28					1.098 (3)	-0.14							1.04	-2.58

[a] Equation (1)
[b] Equation (2)

Species	Al-H bond length	BAC	Al-Cl bond length	BAC	Al-C bond length	BAC	Al-O bond length	BAC	Al-F bond length	BAC	C-H bond length	BAC	Cl-H bond length	BAC	C-O bond length	BAC	O-H bond length	BAC	Atomic[a]	Molecular[b]
AlH_2Cl	1.579 (2)	0.12	2.097	0.92															-1.31	-1.72
$AlHCl_2$	1.568	0.36	2.081(2)	1.21															-2.57	-1.72
HAlCl $^2A'$	1.600	0.26	2.109	1.03															-1.79	-0.86
AlH_2F	1.580 (2)	0.25							1.663	1.99									-2.47	-1.72
	1.565	0.62																		
$AlHF_2$									1.653 (2)	2.42									-4.90	-1.72
HAlF	1.606	0.38							1.667	2.10									-2.96	-0.86
H_2AlOH	1.580	0.03					1.720	0.61									0.968	0.70	-0.55	-2.58
	1.589	0.02																		
	1.577	0.16																		
$HAl(OH)_2$ OALOH cis, trans							1.713	0.77									0.968	0.70	-1.05	-3.44
							1.718	0.76									0.967	0.70		
HAlOH $^2A'$ trans	1.601	0.16					1.726	0.74									0.968	0.70	-1.03	-1.72
$AlH_2(CH_3)$ HCAlH planar	1.594 (2)	0.08			1.961	-0.58					1.092	-0.14							2.01	-3.44
											1.096 (2)	-0.14								

[a] Equation (1)
[b] Equation (2)

Species	Al-H bond length	BAC	Al-Cl bond length	BAC	Al-C bond length	BAC	Al-O bond length	BAC	Al-F bond length	BAC	C-H bond length	BAC	Cl-H bond length	BAC	C-O bond length	BAC	O-H bond length	BAC	Atomic[a]	Molecular[b]
$AlH(CH_3)_2$	1.600	0.27			1.965 (2)	-0.38					1.096 (4)	-0.14							4.06	-5.16
											1.093 (2)	-0.14								
$HAl(CH_3)$ $^2A'$, HAlCH trans	1.608	0.22			1.973	-0.43					1.091	-0.14							1.52	-2.58
											1.096 (2)	-0.14								
$AlFCl_2$			2.065 (2)	1.64					1.648	2.56									-4.99	-1.72
			2.062	1.78					1.646 (2)	2.70										
AlF_2Cl																			-6.16	-1.72
ClAlF			2.097	1.43					1.659	2.39									-4.22	-0.86
$Al(OH)Cl_2$			2.070	1.40			1.701	1.15									0.968	0.70	-3.07	-2.58
			2.080	1.36																
$AlCl(OH)_2$,OAlOH cis, trans			2.082	1.25			1.704	1.04									0.968	0.70	-2.31	-3.44
							1.708	1.02									0.967	0.70		
ClAlOH ,$^2A'$ trans			2.100	1.19			1.717	1.00									0.969	0.70	-2.29	-1.72
$AlCl_2(CH_3)$,HCAlCl planar			2.090 (2)	1.38	1.938	-0.11					1.092	-0.14							-0.52	-3.44
											1.094 (2)	-0.14								

[a] Equation (1)
[b] Equation (2)

Species	Al-H bond length	BAC	Al-Cl bond length	BAC	Al-C bond length	BAC	Al-O bond length	BAC	Al-F bond length	BAC	C-H bond length	BAC	Cl-H bond length	BAC	C-O bond length	BAC	O-H bond length	BAC	Atomic[a]	Molecular[b]
$AlCl(CH_3)_2$			2.115	1.25	1.952 (2)	-0.15					1.095 (4)	-0.14							2.80	-5.16
											1.093 (2)	-0.14								
$AlCl(CH_3)$ trans			2.118	1.19	1.952 (2)	-0.15					1.095 (2)	-0.14							0.26	-2.58
					1.968	-0.20					1.092	-0.14								
$AlF_2(OH)$							1.699	1.41	1.648	2.59							0.967	0.70	-5.40	-2.58
									1.653	2.55										
$AlF(OH)_2$,,FAlOH cis, cis							1.704 (2)	1.17	1.662	2.27							0.966 (2)	0.70	-3.47	-3.44
FAlOH trans							1.718	1.13	1.661	2.28							0.968	0.70	-3.46	-1.72
$Al(OH)_2CH_3$,OAlOH cis, trans					1.948	-0.30	1.718	0.95			1.094 (2)	-0.14					0.968	0.70	1.00	-5.16
							1.724	0.94			1.093	-0.14					0.966	0.70		

[a] Equation (1)
[b] Equation (2)

Species	Al-H bond length	BAC	Al-Cl bond length	BAC	Al-C bond length	BAC	Al-O bond length	BAC	Al-F bond length	BAC	C-H bond length	BAC	Cl-H bond length	BAC	C-O bond length	BAC	O-H bond length	BAC	Atomic[a]	Molecular[b]
$Al(OH)(CH_3)_2$					1.963	-0.24	1.729	0.98			1.094	-0.14					0.967	0.70	3.56	-6.02
					1.955	-0.24					1.096	-0.14								
											1.095 (3)	-0.14								
											1.093	-0.14								
CH_3AlOH, HOAlC cis					1.978	-0.29	1.730	0.93			1.094 (2)	-0.14					0.969	0.70	1.02	-3.44
											1.095	-0.14								
HAl(OH)Cl, ClAlOHcis	1.568	0.27	2.095	1.07			1.707	0.89									0.968	0.70	-1.81	-2.58
$HAl(CH_3)Cl$, HCAlCl trans	1.583	0.32	2.105	1.09	1.948	-0.34					1.093	-0.14							0.74	-3.44
											1.095 (2)	-0.14								

[a] Equation (1)
[b] Equation (2)

Species	Al-H bond length	BAC	Al-Cl bond length	BAC	Al-C bond length	BAC	Al-O bond length	BAC	Al-F bond length	BAC	C-H bond length	BAC	Cl-H bond length	BAC	C-O bond length	BAC	O-H bond length	BAC	Atomic[a]	Molecular[b]
$HAl(OH)CH_3$,CAlOH trans, HCAlO cis	1.595	0.22			1.950	-0.44	1.725	0.80			1.095 (2) 1.093	-0.14 -0.14					0.968	0.70	1.50	-4.30
$Al(OH)CH_3Cl$			2.105	1.23	1.939	-0.21	1.713	1.07			1.094 (2) 1.092	-0.14 -0.14					0.968	0.70	0.24	-4.30
AlO $^2\Sigma$							1.648	1.32											-2.00	-0.86
HAlO $^1\Sigma$	1.573	0.18					1.629	1.25											-1.52	-1.72
H_2AlO $^2B_2$	1.579 (2)	0.03					1.757	0.66											-1.03	-1.72
AlC $^4\Sigma^-$					1.966	0.00					1.089	0.05							-0.42	0.00
AlCH singlet linear					1.946	-0.09													0.07	-1.72
HAlCH HAlCH trans $^2A''$	1.592	0.23			1.882	-0.24					1.086	0.05							0.55	-1.72
$HAlCH_2$ singlet linear C_{2V}	1.574	0.24			1.795	-0.34					1.087 (2)	-0.04							1.04	-2.58
H_2AlCH $^3A''$	1.586 1.588	0.08 0.08			1.896	-0.39					1.080	0.05							1.04	-1.72

[a] Equation (1)
[b] Equation (2)

Species	Al-H bond length	BAC	Al-Cl bond length	BAC	Al-C bond length	BAC	Al-O bond length	BAC	Al-F bond length	BAC	C-H bond length	BAC	Cl-H bond length	BAC	C-O bond length	BAC	O-H bond length	BAC	Atomic[a]	Molecular[b]
AlH_2OCH_3 HCOAl cis	1.589	0.02					1.714	0.83			1.097	-0.15			1.418	-0.29			1.50	-4.30
	1.580	0.03									1.094 (2)	-0.15								

[a] Equation (1)
[b] Equation (2)

TABLE 3. Calculated $\Delta H_f°(0\ K)$ and $\Sigma D_0(0\ K)$ for selected aluminum compounds at various levels of theory (kcal mol^{-1}), with atomic heats of formation at 0 K.

Species	$\Delta H_f°$(0 K) G2	BAC-QCI	BAC-G1	BAC-G2MP2	BAC-G2	BAC-G2 ΣD_0	ΣD_0, literature
AlH_3	30.4	36.4	31.1	32.4	32.5	200.6	200.8 ± 4.8[a], 196.1[c], 201.8[d], 202.7[k]
AlH_2	63.5	66.7	63.6	64.0	64.8	116.7	114.7 ± 4.8[a], 118.0[k]
AlH	57.5	58.3	58.1	57.9	59.3	70.6	70.3 ± 0.4[a], 66.9 ± 4.6[b], 66.1[c], 69.9[d], 73.6[e], 72.9 ± 0.2 [f],< 70.6[g], 72.3[k]
$AlCl_3$	-142.2	-122.2	-138.0	-138.2	-141.1	305.1	303.4 ± 1.5[a]
$AlCl_2$ $^2A_1$	-53.5	-38.7	-50.6	-51.2	-52.2	187.6	192.8 ± 9.6[a]
AlCl $^1\Sigma$	-14.0	-6.7	-12.0	-12.9	-12.0	118.8	119.1 ± 1[a], 118.1[g], 120.8[k]
AlF_3	-286.8	-260.6	-284.2	-279.8	-286.3	419.9	421.8 ± 1.2[a], 391.7[c], 369.6[d]
AlF_2 $^2A'$	-149.7	-129.8	-148.9	-145.1	-148.5	263.7	265.8 ± 7.2[a]
AlF $^1\Sigma$	-64.9	-55.1	-63.9	-62.0	-62.8	159.5	159.9 ± 1.2[a], 160 ± 1.5[b], 152.3[c], 145.1[d], 161.6[e,k],159 ± 3[h], 160.4[i], 162.5[j]
$Al(OH)_3$ C_3 axis	-232.1	-215.3	-232.8	-228.7	-231.1	641.2	649.2 ± 12[a]
$Al(OH)_2$ $^2A_1$ planar, trans, trans	-110.8	-97.1	-112.6	-109.2	-109.9	409.4	419.0 ± 12[a]
AlOH $^1A'$ linear	-44.0	-36.9	-44.2	-42.9	-42.5	231.4	234.3 ± 7.2[a]
$Al(CH_3)_3$	-9.6	1.5	-8.3	-7.5	-7.0	1059.8	
$Al(CH_3)_2$ $^2A'$	37.9	45.1	38.6	38.8	39.9	688.1	
$AlCH_3$ $^1A_1$	43.0	45.9	43.7	43.7	45.2	357.9	
AlH_2Cl	-28.5	-18.2	-26.5	-25.9	-26.7	236.8	234.1 ± 7.2[a]
$AlHCl_2$	-86.6	-71.4	-83.4	-83.3	-85.1	272.1	270.1 ± 7.2[a]
HAlCl $^2A'$	4.2	13.0	5.8	5.6	5.6	152.9	155.4 ± 7.2[a]
AlH_2F	-77.1	-64.4	-75.6	-73.6	-75.4	275.4	274.1 ± 7.2[a]
$AlHF_2$	-184.3	-164.9	-182.2	-179.0	-183.2	350.0	348.5 ± 3.6[a]
HAlF	-43.8	-32.2	-43.4	-41.4	-42.5	190.8	191.4 ± 7.2[a]
H_2AlOH	-57.4	-48.1	-57.1	-55.2	-55.7	347.8	
$HAl(OH)_2$ OAlOH cis, trans	-145.8	-132.6	-145.9	-142.9	-144.4	495.5	
HAlOH $^2A'$ trans	-24.1	-16.2	-24.9	-23.3	-23.0	263.5	
$AlH_2(CH_3)$ HCAlH planar	17.3	24.9	18.3	19.2	19.5	486.9	
$AlH(CH_3)_2$	3.9	13.2	5.2	5.9	6.3	773.3	
$HAl(CH_3)$ $^2A'$ HAlCH trans	50.9	56.1	51.3	51.6	52.6	402.1	
$AlFCl_2$	-190.4	-168.5	-186.9	-185.4	-189.6	343.5	342.5 ± 1.9[a]
AlF_2Cl	-238.7	-214.6	-235.7	-232.6	-238.0	381.8	381.9 ± 1.9[a]

ClAlF	-101.5	-84.3	-99.6	-98.0	-100.2	225.5	229.3 ± 7.2[a], 241 ±15[b]
$Al(OH)Cl_2$	-172.9	-154.3	-170.4	-169.1	-171.8	417.8	418.2 ± 12[a]
$AlCl(OH)_2$ OAlOH cis, trans	-202.9	-185.2	-202.1	-199.3	-201.9	530.0	531.3 ± 12[a]
ClAlOH $^2A'$,trans	-82.5	-68.9	-82.0	-80.6	-81.4	298.8	305.9 ± 9.6[a]
$AlCl_2(CH_3)$ HCAlCl planar	-102.3	-85.6	-98.8	-98.9	-100.5	560.8	
$AlCl(CH_3)_2$	-57.9	-44.3	-55.4	-55.1	-55.6	812.2	
$AlCl(CH_3)$ trans	-10.1	0.7	-8.4	-8.5	-8.4	440.1	
$AlF_2(OH)$	-269.3	-246.2	-267.9	-263.5	-268.6	494.4	497.1 ± 7.2[a]
$AlF(OH)_2$ FAlOH cis, cis	-250.9	-230.4	-250.7	-246.3	-250.0	567.9	571.4 ± 12[a]
FAlOH trans	-130.6	-114.1	-131.0	-127.5	-129.5	336.8	343.6 ± 12[a]
$Al(OH)_2CH_3$ OAlOH cis, trans	-159.9	-145.5	-159.7	-157.0	-158.4	782.7	
$Al(OH)(CH_3)_2$	-85.4	-73.1	-84.2	-83.0	-83.3	921.9	
CH_3AlOH HOAlC cis	-36.6	-27.1	-36.8	-35.4	-35.1	548.8	
HAl(OH)Cl ClAlOH cis	-117.1	-103.2	-115.5	-114.0	-115.6	384.7	
$HAl(CH_3)Cl$ HCAlCl trans	-43.3	-31.2	-41.0	-40.6	-41.2	524.5	
$HAl(OH)CH_3$ CAlOH trans,HCAlO cis	-71.7	-60.7	-70.9	-69.3	-69.7	635.1	
$Al(OH)CH_3Cl$	-132.2	-116.8	-130.4	-129.0	-130.5	672.8	
AlO $^2\Sigma$	18.4	27.7	17.6	19.5	19.9	117.3	121.2 ± 1.2[a], 121.2 ± 2[b], 118.1[e]
HAlO $^1\Sigma$	-2.2	6.3	-1.8	-3.5	-0.4	189.3	187.7 ± 12[a]
H_2AlO $^2B_2$	11.30	20.95	12.05	14.15	13.33	227.2	
AlC $^4\Sigma^-$	171.6	176.3	170.8	169.8	172.1	76.1	86 ± 12[a], 78.6[e], 76.1[l]
AlCH singlet linear	156.7	162.4	157.2	157.1	158.4	141.4	
HAlCH HAlCH trans $^2A''$	124.5	135.1	125.2	129.5	125.7	225.8	
$HAlCH_2$ singlet linear C_{2V}	79.9	87.1	80.9	80.7	81.6	321.5	
H_2AlCH $^3A''$	110.7	119.0	110.7	111.0	111.5	291.6	
AlH_2OCH_3 HCOAl cis	-47.5	-37.3	-46.0	-44.2	-44.9	610.3	
Al	78.23	78.23	78.23	78.23	79.73		
H	51.63	51.37	50.58	50.76	51.15		
Cl	28.59	29.87	30.35	30.03	29.37		
F	18.47	17.92	20.43	20.79	20.41		
O	58.99	56.91	59.31	59.77	59.49		
C	169.98	170.84	168.82	168.45	168.90		

[a] Ref. 2. [b] Ref. 1. [c] D_e, MP2 calculation. See ref. 26. [d] D_e, QCI calculation. See ref. 26. [e] CCSD(T)/WMR calculation. See ref. 27. [f] Baltayan, P.; Nedelec, O. *J. Chem. Phys*. **1979**, *70*, 2399. [g] Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*, Van Nostrand: New

York, 1979. [h] Murad, E.; Hindenbrand, D. L.; Main, R. P. *J. Chem. Phys*. **1966**, *45*, 263. [i] D_e, MP4SDQ calculation; Peterson, K. A., Woods, R. C. *J. Chem. Phys.* **1988**, *89*, 4929. [j] MP4/6-311+G(MC)(3d2f) calculation. See ref. 28. [k] G2 calculation; Ref. 6. [l] MRCI calculation. See ref. 29.

TABLE 4. $\Delta H_f°$ (298 K) for the BAC-G2 Level of Theory with Error Estimates and Literature Values for Selected Aluminum Compounds (kcal mol^{-1}).

Species	ΔH_f^o	JANAF[b]	Gurvich[a]	Other sources
AlH_3	30.9 ± 1.8		30.8 ± 4.8	26.9[d], 24.2[e], 13.6[f], 84.5[g], 30.6[h], 29.5[i], 29.1[u]
AlH_2	64.1 ± 1.8		66.2 ± 4.8	51.8[d], 50.4[e], 45.4[f], 10.7[g], 61.8[h], 62.4[i], 63.5[j], 63.4[t], 63.1[u]
AlH	59.2 ± 2.0	61.9 ± 4.8	59.6 ± 0.8	63.0[d], 46.0[e], 52.9[f], 70.1[g], 59.5[h], 58.2[i], 58.6[t], 57.7[u]
$AlCl_3$	-141.5 ± 4.4	-139.7 ± 0.7	-139.7 ± 1.2	-142.5,[c] -134.3[k], -140 ± 0.43[l], -149.2[d], -140.3[e], -140.3[f], -122.1[g], -126.8[h], -146.3[i], -139.4,[m] -146.4[t], -139.8[u]
$AlCl_2$ $^2A_1$	-52.4 ± 2.1	-66.9 ± 4.8	-57.6 ± 9.6	-71.4[d], -74.6[e], -74.0[f], -68.2[g], -46.8[h], -57.4[i], -57.3[j], -79.1[m], -57.4[t], -51.8[u]
AlCl $^1\Sigma$	-11.9 ± 1.3	-12.3 ± 1.5	-12.2 ± 0.7	-12.7[d], -27.8[e], -20.8[f], -5.5[g], -9.1[h], -15.4[i], -11.4[m], -15.4[t], -12.9[u]
AlF_3	-287.1 ± 6.9	-289.0 ± 0.6	-289.0 ± 0.7	-287.6,[c] -291.9[d], -291.3[e], -285.8[f], -291.5[g], -287.9[m], -290.4[t], -286.2[v]
AlF_2 $^2A'$	-148.9 ± 3.6	-166.1 ± 9.6	-151.0 ± 7.2	-152.4[t]
AlF $^1\Sigma$	-62.8 ± 1.7	-63.5 ± 0.8	-63.1 ± 0.7	-65.7[d], -83.6[e], -77.9[f], -50.1[g], -61.7[m], -65.4[t]
$Al(OH)_3$ C_3 axis	-233.8 ± 3.1		-242.0 ± 12	
$Al(OH)_2$ $^2A_1$ planar, trans, trans.	-111.5 ± 2.9		-121.3 ±12	
AlOH $^1A'$ linear	-42.8 ± 2.0	-43.0 ± 3.1	-46.1 ±7.2	-34.5[d], -61.1[e], -40.1[f], -33.4[g], -40.0[h], -45.5[i], -44.7[t], -43.8[u]
$Al(CH_3)_3$	-12.8 ± 1.6			-19.4[n], -20.5[d], -40.1[e], -27.5[f], -5.7[g], -17.8[m], -20.9[o], -5.6[p], -13.1[q]
$Al(CH_3)_2$ $^2A'$	36.2 ± 2.0			
$AlCH_3$ $^1A_1$	43.6 ± 2.4			
AlH_2Cl	-28.1 ± 1.3		-25.4 ± 7.2	-24.1[h], -30.7[i], -28.8[u]
$AlHCl_2$	-86.1 ± 2.7		-84.0 ± 7.2	-77.1[h], -89.8[i], -89.4[t], -85.6[u]
HAlCl $^2A'$	5.0 ± 1.0		2.5 ± 7.2	6.1[h], 1.5[i], 1.6[j], 4.7[u]
AlH_2F	-76.9 ± 2.1		-75.7 ± 7.2	
$AlHF_2$	-184.4 ± 4.4		-182.9 ± 3.6	
HAlF	-43.1 ± 1.8		-43.6 ± 7.2	
H_2AlOH	-57.9 ± 1.8			
$HAl(OH)_2$ OAlOH cis, trans	-146.9 ± 2.3			
HAlOH $^2A'$ trans	-24.3 ± 2.2			
$AlH_2(CH_3)$ HCAlH planar	16.4 ± 1.6			
$AlH(CH_3)_2$	1.7 ± 1.6			-6.4[o], 6.2[p], 0.9[q]
$HAl(CH_3)$ $^2A'$ HAlCH trans	50.3 ± 1.9			

$AlFCl_2$	-190.1 ± 5.0	-189.0 ± 1.4	-189.1 ± 1.7	-195.4[d], -191.4[e], -186.7[f], -178.0[g]
AlF_2Cl	-238.7 ± 5.9	-238.8 ± 1.5	-238.8 ± 1.7	-243.0[d], -241.6[e], -236.2[f], -234.6[g]
ClAlF	-100.5 ± 2.5	-117.0 ± 15.1	-104.3 ± 7.2	-104.6[t]
$Al(OH)Cl_2$	-173.0 ± 3.3		-173.3 ± 12	
$AlCl(OH)_2$ OAlOH cis, trans	-203.8 ± 2.8		-205.3 ± 12	
ClAlOH $^2A'$ trans	-82.3 ± 1.4		-89.3 ± 9.6	-86.0[t]
$AlCl_2(CH_3)$ HCAlCl planar	-102.7 ± 2.6			-119.7±1.7[o]
$AlCl(CH_3)_2$	-59.6 ± 1.1			-79.9±2.1[o]
$AlCl(CH_3)$ trans	-10.3 ± 1.0			
$AlF_2(OH)$	-270.0 ± 5.2		-273.8 ± 9.6	
$AlF(OH)_2$ FAlOH cis, cis	-252.0 ± 3.9		-255.6 ± 12	
FAlOH trans	-130.5 ± 2.7		-137.2 ± 12	-133.5[t]
$Al(OH)_2CH_3$ OAlOH cis, trans	-162.1 ± 2.1			
$Al(OH)(CH_3)_2$	-88.1 ± 1.4			
CH_3AlOH HOAlC cis	-37.8 ± 2.0			
HAl(OH)Cl ClAlOH cis	-117.4 ± 1.9			
$HAl(CH_3)Cl$ HCAlCl trans	-44.0 ± 1.2			
$HAl(OH)CH_3$ CAlOH trans,HCAlO cis	-73.3 ± 1.6			
$Al(OH)CH_3Cl$	-133.5 ± 1.8			
AlO $^2\Sigma$	19.9 ± 2.6	15.9 ± 1.9	16.1 ± 1.5	3.9[d], -1.8[e], 8.4[f], 9.8[g], 18.9[h], 17.0[i], 18.8[j], 21.8[m], 18.9[t], 18.8[u]
HAlO $^1\Sigma$	-1.1 ± 3.5	8.0 ± 20.1	0.4 ± 12	189.9[h], 189.9[i], -5.3[t]
H_2AlO $^2B_2$	11.9 ± 1.8			
AlC $^4\Sigma^-$	172.9 ± 2.8	164.8 ± 2.4	163.1 ± 12	172.5[h], 171.5[i], 171.7[j], 172.8[u]
AlCH singlet linear	158.6 ± 2.0			
HAlCH HAlCH trans $^2A''$	125.2 ± 4.0			
$HAlCH_2$ singlet linear C_{2V}	80.5 ± 1.6			
H_2AlCH $^3A''$	110.6 ± 1.4			
AlH_2OCH_3 HCOAl cis	-48.5 ± 1.6			
CH_3	34.77 ± 1.00	34.82 ± 0.19		35.06 ± 0.10[r]
CH_2	93.63 ± 1.04	92.35 ± 1.00		
CH	141.18 ± 1.02	142.00 ± 4.18		
OH	9.23 ± 1.01	9.3 ± 0.29		8.89 ± 0.09[s]
C	170.13 ± 1.10	171.29 ± 0.11		
O	59.93 ± 1.05	59.55 ± 0.02		
Cl	29.75 ± 1.55	28.99 ± 0.0019		

F	20.84 ± 1.07	18.98 ± 0.07	
H	51.59 ± 1.21	52.10 ± 0.0014	
Al	80.14 ± 2.35	78.80 ± 1.00	78.87 ± 0.72

[a] Ref. 2. [b] Ref. 1. [c] G2, calculation uncorrected for atomic spin-orbit effects. See ref. 6. [d] MNDO/d calculation. See ref. 30. [e] MNDO calculation. See ref 30. [f] AM1 calculation. See ref. 30. [g] PM3 calculation. See ref. 30. [h] B3LYP calculation. See ref. 11. [i] CBS-Q calculation. See ref. 11. [j] CBS-RAD calculation. See ref. 11. [k] K2-BVWN calculation. See ref. 31. [l] Ref. 32. [m] Ref. 3. [n] Ref. 33. [o] Ref. 34. [p] B3LYP/6-311++G(2df,pd) calculation. See ref. Simka, H.; Willis, B. G.; Lengyel and, I.; Jensen, K. F. *Prog. Crystal Growth and Charact.* , **1997**, *35*, 117; Willis, B. G.; Jensen, K. F. *J. Phys. Chem. A* **1998**, *102*, 2613. [q] G2MP2 calculation. See footnote (p). [r] Dobis, O.; Benson, S. W. *Int. J. Chem. Kinet.* **1987**, *19*, 691. [s] Rusic, B.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Harding, L. B.; Asher, R. L.; Wagner, A. F. *J. Phys. Chem. A*, **2001**, *105*, 1. [t] Ref. 35. [u] Spin-orbit-corrected G2 calculation. See ref. 11. [v]Spin-orbit-corrected G2 calculation. See ref. 10.

Table 5: Thermochemistry Parameters at Various Temperatures (K).

	ΔH_f^o [a]	S^o [b]	ΔG_f^o [a]					
Species	298	298	300	600	1000	1500	2000	2500
AlH_3	30.9	49.7	27.3	15.1	36.9	42.4	48.0	53.6
AlH_2	64.1	51.1	55.4	38.0	52.8	49.8	47.2	44.8
AlH	59.2	44.9	47.7	27.4	38.1	30.1	22.5	15.2
$AlCl_3$	-141.5	75.4	-142.9	-153.4	-130.0	-122.5	-114.8	-107.1
$AlCl_2$ $^2A_1$	-52.4	69.4	-60.0	-76.5	-60.8	-62.8	-64.2	-65.5
AlCl $^1\Sigma$	-11.9	54.6	-23.0	-43.1	-32.0	-39.6	-46.6	-53.3
AlF_3	-287.1	66.6	-288.0	-297.9	-273.4	-264.7	-255.7	-246.6
AlF_2 $^2A'$	-148.9	63.4	-156.1	-172.2	-155.9	-156.9	-157.5	-157.9
AlF $^1\Sigma$	-62.8	51.4	-73.7	-93.5	-82.0	-89.1	-95.6	-101.8
$Al(OH)_3$ C_3 axis	-233.8	74.0	-222.8	-220.7	-180.6	-152.6	-125.9	-99.7
$Al(OH)_2$ $^2A_1$ planar, trans, trans	-111.5	68.1	-110.6	-118.6	-91.7	-80.3	-69.0	-57.9
AlOH $^1A'$ linear	-42.8	49.6	-48.4	-62.8	-44.3	-42.4	-40.0	-37.4
$Al(CH_3)_3$	-12.8	94.6	-0.7	2.6	45.9	78.4	110.2	140.9
$Al(CH_3)_2$ $^2A'$	36.2	80.1	38.3	31.6	61.3	77.0	92.6	107.6
$AlCH_3$ $^1A_1$	43.6	57.2	38.1	24.2	44.0	47.6	51.6	55.7
AlH_2Cl	-28.1	60.7	-31.7	-44.1	-22.7	-17.7	-12.5	-7.4
$AlHCl_2$	-86.1	69.3	-89.0	-100.7	-78.8	-73.2	-67.3	-61.5
HAlCl $^2A'$	5.0	61.8	-3.6	-21.0	-6.4	-9.6	-12.4	-15.0
AlH_2F	-76.9	57.7	-80.3	-92.4	-70.6	-65.1	-59.5	-53.8
$AlHF_2$	-184.4	63.4	-186.9	-198.2	-175.6	-169.0	-162.3	-155.5
HAlF	-43.1	58.8	-51.5	-68.7	-53.8	-56.5	-58.9	-61.0
H_2AlOH	-57.9	60.9	-57.5	-65.9	-39.2	-27.7	-16.2	-5.1
$HAl(OH)_2$ OAlOH cis, trans	-146.9	68.7	-141.6	-145.1	-112.2	-93.2	-74.6	-56.6
HAlOH $^2A'$ trans	-24.3	60.7	-28.6	-41.6	-21.2	-17.2	-13.2	-9.3
$AlH_2(CH_3)$ HCAlH planar	16.4	69.0	16.7	8.4	35.7	48.0	60.3	72.2
$AlH(CH_3)_2$	1.7	81.4	8.1	5.7	41.2	63.8	86.1	107.6
$HAl(CH_3)$ $^2A'$ HAlCH trans	50.3	65.3	47.0	35.1	57.5	64.0	70.6	77.1
$AlFCl_2$	-190.1	74.7	-192.0	-202.9	-180.1	-173.3	-166.3	-159.3
AlF_2Cl	-238.7	71.7	-240.4	-251.1	-227.9	-220.7	-213.3	-205.8
ClAlF	-100.5	67.8	-108.3	-125.0	-109.6	-111.8	-113.6	-115.1
$Al(OH)Cl_2$	-173.0	78.2	-171.2	-178.5	-150.8	-138.2	-125.8	-113.6
$AlCl(OH)_2$ OAlOH cis, trans	-203.8	77.3	-197.8	-200.7	-167.3	-147.7	-128.7	-110.1
ClAlOH $^2A'$ trans	-82.3	70.0	-86.1	-98.8	-78.0	-73.9	-69.6	-65.3
$AlCl_2(CH_3)$ HCAlCl planar	-102.7	86.2	-101.0	-108.2	-79.9	-66.2	-52.6	-39.4
$AlCl(CH_3)_2$	-59.6	89.0	-52.2	-53.7	-17.3	6.5	30.0	52.7
$AlCl(CH_3)$ trans	-10.3	74.8	-13.1	-24.8	-2.1	4.8	11.8	18.7
$AlF_2(OH)$	-270.0	72.3	-267.9	-274.7	-246.3	-233.0	-219.8	-206.7
$AlF(OH)_2$ FAlOH cis, cis	-252.0	74.7	-245.9	-248.7	-214.9	-195.5	-176.4	-157.5
FAlOH trans	-130.5	67.0	-134.1	-146.5	-125.4	-120.7	-115.9	-111.1
$Al(OH)_2CH_3$ OalOH cis, trans	-162.1	84.4	-151.8	-150.4	-110.6	-83.0	-56.1	-30.1
$Al(OH)(CH_3)_2$	-88.1	89.6	-76.9	-74.4	-32.9	-3.1	26.1	54.4
CH_3AlOH HOAlC cis	-37.8	77.2	-37.3	-45.6	-18.6	-6.5	5.4	16.9
HAl(OH)Cl ClAlOH cis	-117.4	69.5	-116.3	-124.1	-97.0	-85.0	-73.0	-61.0
$HAl(CH_3)Cl$ HCAlCl trans	-44.0	76.7	-42.7	-50.2	-22.0	-8.5	4.9	18.0
$HAl(OH)CH_3$ CAlOH trans, HCAl cis	-73.3	74.2	-67.2	-69.9	-35.4	-14.3	6.7	27.2
$Al(OH)CH_3Cl$	-133.5	82.9	-126.7	-128.9	-93.8	-72.0	-50.4	-29.6

	ΔH_f^o [a]	S^o [b]	ΔG_f^o [a]					
Species	298	298	300	600	1000	1500	2000	2500
AlO $^2\Sigma$	19.9	52.4	8.8	-11.2	-0.2	-7.9	-15.1	-22.0
HAlO $^1\Sigma$	-1.1	52.9	-7.7	-23.1	-6.0	-6.3	-6.4	-6.4
H_2AlO $^2B_2$	11.9	59.26	8.1	-4.5	16.5	20.9	25.5	30.1
AlC $^4\Sigma^-$	172.9	54.0	154.4	126.8	127.8	107.8	88.6	69.8
AlCH singlet linear	158.6	40.5	148.8	130.1	143.0	138.0	133.8	129.9
HAlCH HAlCH trans $^2A''$	125.2	61.0	114.0	93.9	104.7	96.6	88.9	81.3
$HAlCH_2$ singlet linear C_{2V}	80.5	61.8	73.6	58.1	75.4	75.5	76.0	76.4
H_2AlCH $^3A''$	110.6	65.9	102.5	85.5	100.6	97.8	95.1	92.3
AlH_2OCH_3 HCOAl cis	-48.5	72.1	-41.8	-43.5	-7.5	15.7	38.6	60.7

[a] In kcal mol^{-1}. [b] In cal mol^{-1} K^{-1}.

Table 3 reveals the trend toward convergence in each molecule as the level of theory increases from BAC-QCI to BAC-G2. In most cases, the calculation appears to be converged at the BAC-G2MP2 level, there being little difference in the heats of formation predicted at the BAC-G2MP2 and BAC-G2 levels. Exceptions to this almost exclusively involve fluorinated compounds. For example, the heat of formation of AlF_3 at the BAC-G2 level is 8.5 kcal mol^{-1} lower than at the BAC-G2MP2 level. This behavior is reflected in the relatively large uncertainty in the predicted heats of formation of the fluorinated species (Table 4). Table 3 also indicates that differences between BAC-G2 predictions and G2 itself are, for the most part, small. The largest difference, 2.6 kcal mol^{-1}, is for $Al(CH_3)_3$, which might be expected since this is the largest molecule included in the study. As discussed above, it is in the prediction of thermochemistry for large polyatomics where the value of the BAC approach is expected to be most clear. Finally, Table 3 includes the BAC-G2 atomization energies (ΣD_0; calculated from the BAC-G2 molecular heats of formation and the experimental[1] atomic heats of formation at 0 K) for comparison with the results of other computational studies in which the heat of formation was not calculated.

Trends in heats of formation (298 K) as a function of the number of ligands of a specific type are shown in Figures 1—4. There are several noteworthy observations. The most general one is that, in all cases, replacement of one ligand with another within a homologous series (i.e., AlX_nY_{3-n}, n = 0—3) results in a linear change in the heat of formation. Deviations from perfect linearity (based on a least-squares fit) are less than 1 kcal mol^{-1} in most cases. The series closest to perfect linearity is $AlH_n(CH_3)_{3-n}$ (maximum deviation < 0.1 kcal mol^{-1}), while those displaying the largest deviations are $AlCl_n(CH_3)_{3-n}$ and AlH_nF_{3-n} (maximum deviation ~ 2 kcal mol^{-1}). This confirms the essentially local nature of the bonding within these compounds, i.e., the interaction between aluminum and a given atom or group is largely unaffected by its neighbors, while confirming that interactions between chlorine and methyl groups may occur, as was observed previously in silicon compounds.[19] It is unclear whether the higher deviation seen for the fluorine substitution of hydrogen is due to non-localized bonding or poor performance of the G2 method. Notably, however, the $Al(OH)_nF_{3-n}$ and $AlCl_nF_{3-n}$ series both have low maximum deviations (< 0.5 kcal mol^{-1}) suggesting that the non-linearity is due to a bonding interaction in the aluminum fluorohydrides and not to the G2 method itself. We have found few exceptions to linearity in our previous examinations of Group-III and Group-IV chemistry; examples include the $SiH_{4-n}(OH)_n$[20] and $SiCl_{4-n}(CH_3)_{4-n}$ homologous series.

The remaining conclusions we draw from Figure 1—4 concern the relative stability of the various ligands. First, as can be seen in Figure 1, replacing H with any of the other four ligands (CH_3, OH, F, or Cl) results in increased molecular stability, since the heat of formation always decreases as the number of non-hydrogen ligands increases. The slopes of the four lines in Figure 1 are -106.2 kcal mol^{-1} for substitution by F, -88.3 kcal mol^{-1} for substitution by OH, -57.5 kcal mol^{-1} for substitution by Cl, and -14.6 kcal mol^{-1} for substitution by CH_3. In contrast, substitution of OH by anything except F results in molecular destabilization, since the heats of formation increase with increasing numbers of non-OH ligands (Figure 2). Replacing OH with F decreases $\Delta H_f°$ by 17.8 kcal mol^{-1}. Trends produced by replacing CH_3 (Figure 3) and Cl (Figure 4) fall

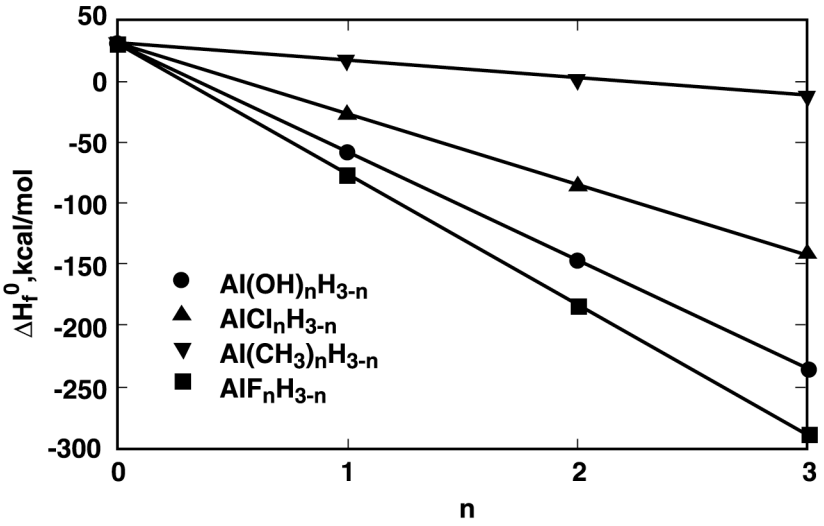

Figure 1. BAC-G2 heats of formation for substitution of H by R in the series AlH_nR_{3-n}, R = OH, F, Cl, CH_3; n = 0 - 3.

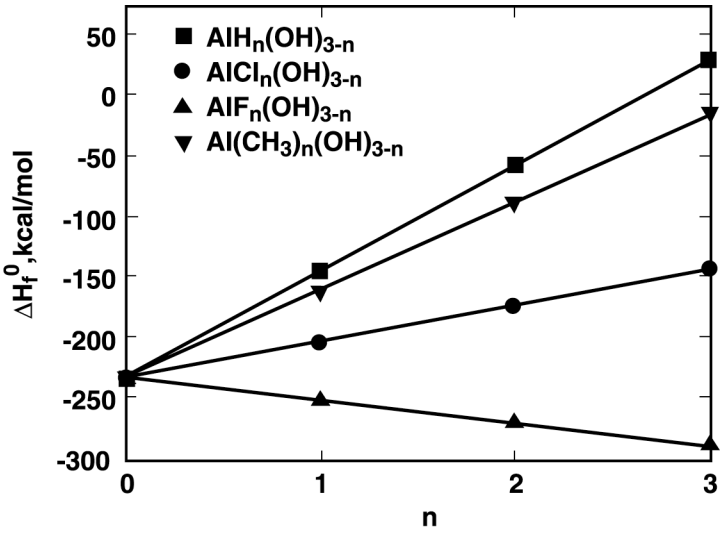

Figure 2. BAC-G2 heats of formation for OH substitution in the series $AlR_n(OH)_{3-n}$, R = H, CH_3, F, Cl; n = 0 - 3.

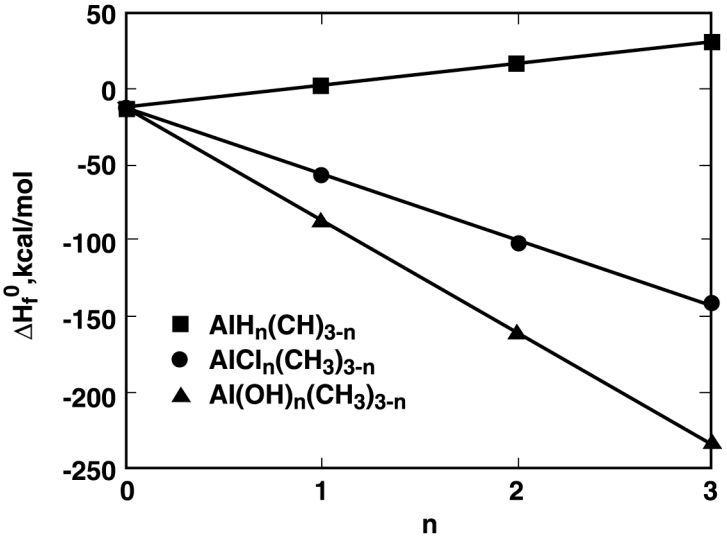

Figure 3. BAC-G2 heats of formation for substitution of CH_3 by R in the series $AlR_n(CH_3)_{3-n}$, R = H, Cl, OH; n = 0 - 3.

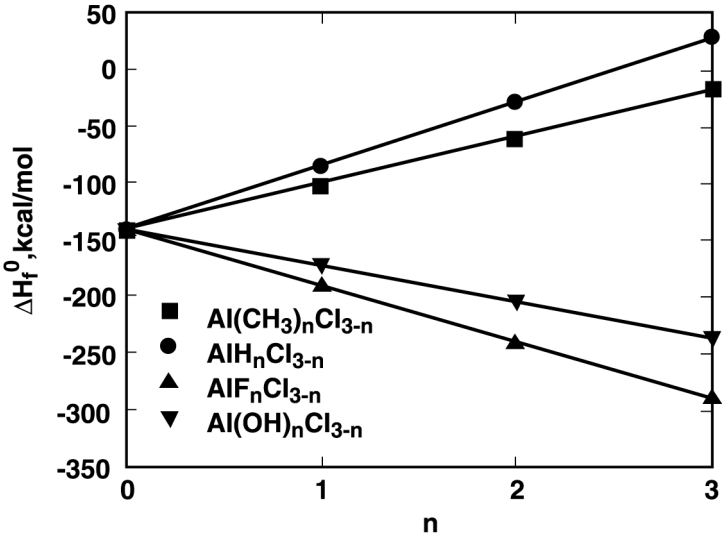

Figure 4. BAC-G2 heats of formation for chlorine substitution in the series AlR_nCl_{3-n}, R = H, OH, F, CH_3; n = 0 - 3.

between these extremes. For example, replacing Cl by either OH or F results in stabilization, by 30.8 kcal mol^{-1} and 48.5 kcal mol^{-1}, respectively. Thus, as one might expect, the overall trend in molecular stability is F > OH > Cl > CH_3 > H.

Bond dissociation energies (BDE) , which can be calculated from the molecular and atomic heats of formation given in Table 4, generally reflect the trends in heats of formation discussed above. The calculations predict increasing Al-ligand bond strengths in the order H ~ CH_3 < Cl < OH < F. For trivalent species, the Al-H and Al-CH_3 bond energies are comparable, falling in the range 83 - 88 kcal mol^{-1}. Bonds to Cl are considerably stronger, with values of 118—125 kcal mol^{-1}. Bonds to OH are even stronger, with some dissociation energies approaching 134 kcal mol^{-1}. Finally, Al-F BDEs are by far the strongest, with values as high as 160 kcal mol^{-1}. These results are consistent with the fact that lower deposition temperatures are required when, for example, oxides are deposited by CVD from organoaluminum instead of halogenated compounds.[36,37]

These results indicate that bonds to aluminum are generally weaker than those to boron. For example, B-H bonds in trivalent boron compounds are on the order of 105 kcal mol^{-1}.[21] Bonds between aluminum and methyl groups are also significantly weaker than their boron counterparts, as discussed previously.[13] Dissociation of the first Al-CH_3 bond in trimethylaluminum is more than 20 kcal mol^{-1} weaker than the same bond in trimethylborane. Dissociation energies for bonds between boron and chlorine,[21] however, are very similar to those between aluminum and chlorine. Data for boron hydroxides are sparse, but heats of formation reported by Gurvich et al.[2] indicate that the analogous aluminum bonds are weaker as well. These comparisons are consistent with the general trends in main-group bond energies, which decrease as one proceeds down the periodic table from the first to the fourth row.[13]

Ligand substitution in trivalent aluminum compounds has very little effect on bond dissociation energies in these compounds. In general exchanging one ligand for another changes the BDE of the remaining ligands of that type by less than 1 kcal mol^{-1}. Increasing the number of halogen atoms in a molecule generally reduces the Al-halogen BDE, although the BDEs of the other ligands are not changed by more than ~ 2 kcal mol^{-1}. These observations are consistent with the trends in heats of formation discussed above, again showing that bonding in these compounds is highly localized.

This localized behavior does not extend to non-trivalent compounds, however. In particular, the effect on the BDE of exchanging ligands in divalent species is much more profound. The unpaired electron in AlXY compounds is strongly affected by the electronegativity of the ligands. If electronegativities of the exchanged ligands are substantially different, e.g., when replacing H or CH_3 by Cl, F, or OH, a considerable redistribution of the electron density occurs, with the unpaired electron going to the more electronegative atom. This makes the bond to the electronegative ligand much stronger than the bond to the more electropositive ligand. This effect can be clearly seen in Table 6. For example, when substituting F for H in AlH_2 to form HAlF, the Al-H BDE drops from 46.7 kcal mol^{-1} to 31.9 kcal mol^{-1}. In contrast, substitution of CH_3 for H in AlH_2 decreases the Al-H BDE by less than 2 kcal mol^{-1}.

Table 6: Calculated Bond Dissociation Enthalpies (BDE) at 298 K for Selected Aluminum Compounds (kcal mol^{-1}).

Species	BDE					
	Al-H	Al-C	Al-O	Al-Cl	Al-F	C-O
AlH_3	84.8					
AlH_2	46.7					
AlH	72.5					
$AlCl_3$				118.9		
$AlCl_2$ $^2A_1$				70.3		
AlCl $^1\Sigma$				121.8		
AlF_3					159.0	
AlF_2 $^2A'$					106.9	
AlF $^1\Sigma$					163.8	
$Al(OH)_3$ C_3 axis			131.5			
$Al(OH)_2$ $^2A_1$ planar, trans, trans			77.9			
AlOH $^1A'$ linear			132.2			
$Al(CH_3)_3$		83.8				
$Al(CH_3)_2$ $^2A'$		42.2				
$AlCH_3$ $^1A_1$		71.3				
AlH_2Cl	84.7			122.0		
$AlHCl_2$	85.3			120.9		
HAlCl $^2A'$	34.7			84.0		
AlH_2F	85.4				161.8	
$AlHF_2$	87.1				162.1	
HAlF	31.9				123.1	
H_2AlOH	85.2		131.2			
$HAl(OH)_2$ OAlOH cis, trans	87.0		131.8			
HAlOH $^2A'$ trans	33.1		92.7			
$AlH_2(CH_3)$ HCAlH planar	85.5	82.5				
$AlH(CH_3)_2$	86.1	83.4				
$HAl(CH_3)$ $^2A'$ HAlCH trans	44.9	43.7				
$AlFCl_2$				119.4	158.5	
AlF_2Cl				119.6	159.0	
ClAlF				67.5	109.4	
$Al(OH)Cl_2$			129.8	120.5		
$AlCl(OH)_2$ OAlOH cis, trans			130.7	122.1		
ClAlOH $^2A'$ trans			79.6	69.3		
$AlCl_2(CH_3)$ HCAlCl planar		85.1		122.2		
$AlCl(CH_3)_2$		84.1		125.6		
$AlCl(CH_3)$ trans		33.2		83.7		
$AlF_2(OH)$			130.3		160.3	
$AlF(OH)_2$ FAlOH cis, cis			130.7		161.3	
FAlOH trans			76.9		108.5	
$Al(OH)_2CH_3$ OAlOH cis, trans		85.4	133.5			
$Al(OH)(CH_3)_2$		85.1	133.5			
CH_3AlOH HOAlC cis		29.8	90.6			
HAl(OH)Cl ClAlOH cis	86.7		131.6	122.9		
$HAl(CH_3)Cl$ HCAlCl trans	85.3	83.8		124.1		
$HAl(OH)CH_3$ CAlOH trans, HCAlO cis	87.1	83.8	132.8			
$Al(OH)CH_3Cl$		86.0	132.4	125.5		
AlO $^2\Sigma$			120.2			
HAlO $^1\Sigma$	72.6		120.2			

Species	BDE					
	Al-H	Al-C	Al-O	Al-Cl	Al-F	C-O
H_2AlO $^2B_2$	38.6		112.1			
AlC $^4\Sigma^-$		77.4				
AlCH singlet linear		62.7				
HAlCH HAlCH trans $^2A''$	85.0	75.2				
$HAlCH_2$ singlet linear C_{2V}		72.3				
H_2AlCH $^3A''$	66.2	94.7				
AlH_2OCH_3 HCOAl cis						95.2

Successive removal of ligands within a given molecule results in a high-low-high trend in BDEs that is displayed by silicon compounds (see for example Ref. 20) as well as other Group III compounds.[21] For example, the Al-Cl BDE in $AlCl_3$, $AlCl_2$, and AlCl, are 118.1 kcal mol^{-1}, 69.5 kcal mol^{-1}, and 119.7 kcal mol^{-1}, respectively. This trend is evident for all five ligands examined in this study. The stronger bond in AlX_3 relative to AlX_2 species is a consequence of the energy penalty paid for unpairing electrons, resulting in a product with a doublet ground state. Alternatively, breaking the Al-X bond in AlX_3 requires less energy, since there is a thermodynamic advantage to pairing the valence electrons on aluminum (all AlX species have $^1\Sigma$ ground states).

B. Comparisons with experimental data. The BAC-G2 heats of formation for the aluminum hydrides, fluorides , and chlorides are generally in good agreement with the primary critical reviews of thermodynamic data, Gurvich et al.,[2] and the JANAF Tables.[1] In particular, the BAC-G2 value is good agreement with the data in these reviews, as well as other sources,[3,32] for $AlCl_3$ and AlF_3. This is encouraging, since the experimental data for these compounds are probably the most accurate of those available for aluminum-containing species. The biggest disagreements occur for the divalent species, whose heats of formation in the critical reviews were obtained through estimation techniques. The agreement is particularly poor with the JANAF heats of formation (differences as large as 15 kcal mol^{-1} for $AlCl_2$) and indicates that the JANAF values are likely in error. Data for AlH_3 and $AlCl_2$ from the older NBS Tables[3] also do not agree well with the BAC-G2 values. The estimated values reported by Gurvich et al. for the divalent species are in much better agreement with the BAC-G2 values. Predicted values for the diatomics AlH, AlF, and AlCl are in quite good agreement with the standard sources. Values for mixed halide/hydride species (i.e., AlH_nX_{3-n}, X = F, Cl; n = 1—3) estimated by Gurvich et al. for the most part agree well with theory. This is not surprising, since the linear estimations used by those authors are consistent with the observation (discussed earlier) that bonding in these compounds appears to be quite localized.

Unfortunately, data for organometallic aluminum compounds are quite thin, although several sources report a heat of formation for trimethylaluminum.[3,33,34] The value in the *NBS Tables* (-17.8 kcal mol^{-1})[3] and the value preferred by Cox and Pilcher (-20.9 ± 1.7)[4] are significantly lower than the BAC-G2 value of –12.8 kcal mol^{-1}. Cox and Pilcher list an alternate measurement obtained by Long and Norrish[38] (-13.6 ± 2.5 kcal mol^{-1}) that is actually in better agreement with the calculation. A more recent compilation by Pilcher and Skinner[33] gives –19.4 kcal mol^{-1}. An estimated heat of formation for $AlH(CH_3)_2$ reported by Smith (-6.4 kcal mol^{-1}) does not agree well with the BAC-G2 value.[34] Thus, none of the reported values is in particularly good agreement with the BAC-G2 prediction, suggesting that additional experimental and theoretical investigations should be performed to add confidence to the theoretical result.

Data for oxygen-containing aluminum compounds are also rare, making it difficult to validate model predictions. The diatomic molecule AlO is the only species that can be considered well characterized. Heats of formation for AlO in both *JANAF* and Gurvich et al. are lower than the BAC-G2 prediction by about 4 kcal mol^{-1}. The only trivalent compound with a reported heat of formation is $Al(OH)_3$, for which the Gurvich et al. report an estimated value of –242 kcal mol^{-1} and the *NBS Tables* report –305 kcal mol^{-1}.[3] Both values are in serious disagreement with the BAC-G2 prediction of -233.8 kcal mol^{-1}. Estimated heats of formation

given by Gurvich et al. for $Al(OH)_2$ and AlOH also do not agree well with the theory (Table 4). The *JANAF Tables* report a heat of formation for HAlO nearly 9 kcal mol^{-1} higher than the BAC-G2 prediction. The estimation techniques employed by Gurvich et al. and *JANAF* involved average bond energies in various aluminum compounds (including halides as well as oxygen-containing compounds), so it is not surprising that a substantial error could result. As in the case of the organometallic compounds, additional experimental data are required to fully validate the computational predictions for aluminum-oxygen compounds, although it seems likely that the data in the *NBS Tables* for $Al(OH)_3$ are in error.

C. Comparisons with other quantum-chemistry predictions. Although it is not the purpose of this article to perform a comprehensive review of theoretical treatments of aluminum compounds, it is enlightening to compare the results of selected methods that have been published with the predictions of the BAC-G2 method. Heats of formation for aluminum-containing compounds obtained from quantum-chemistry techniques are more numerous than experimental data. Methods including semi-empirical techniques,[30] density functional theory (DFT),[11,31,39,40] and high-level calculations[6,7,11,13,26-29,31,35,39,41] have been employed, although none of these studies treats as large a set of molecules as are examined here.

We will not discuss the uncorrected G2 results (Table 3) further, since these have already been discussed here and by other investigators.[6,7,11,42] However, we remark that G2 predictions for aluminum halides that are both corrected[10,11] and uncorrected[7] for atomic spin-orbit energies exist in the literature, which can lead to some confusion regarding the accuracy of this method. The BAC-G2 method does not explicitly correct for the atomic spin-orbit interaction (which would be accomplished by adding experimental spin-orbit interaction energies to the raw G2 atomic energies used in the calculation of the heat of atomization, ΣD_0). Instead, the BAC-G2 atomic corrections implicitly account for spin-orbit interactions that may exist. It is worth noting that, while applying atomic spin-orbit corrections improves the agreement between the G2 prediction and experiment for $AlCl_3$, this actually makes the agreement worse for AlF_3.[10] This reflects the fact that errors in G2 heats of formation for halogenated species are not purely caused by the lack of spin-orbit corrections, but are also due to factors such as basis-set superposition errors, which are evidently more serious in compounds of fluorine than of chlorine.

The most comprehensive investigations prior to this one in which a high-level quantum-chemistry method was applied to a series of aluminum compounds are those of Swihart and Catoire (SC)[11] and Politzer et al.,[35] each of whom examined a series of compounds expected to be present during combustion of aluminum to form particles. SC used two complete basis set methods (CBS-Q and CBS-RAD) as well as DFT (discussed below). Politzer et al. used CBS-QB3 calculations exclusively. In both cases, the CBS methods are generally in agreement with both experiment and the BAC-G2 predictions, but the predicted heats of formation are almost uniformly more negative than both. The poor performance with regard to chlorides is also noteworthy; this has already been remarked with regard to polychlorides in general.[10] The only instance in which the CBS prediction is more positive than the BAC-G2 value is the heat of formation reported by SC for HAlO. In this case, the value of 189.9 kcal mol^{-1} differs considerably from the BAC-G2 value (-1.1 kcal mol^{-1}). Personal communication with the authors of Ref. 11 indicates that this disagreement is due to an error in converting the G2 results to a heat

of formation; the correct G2 heat of formation at 298 K for HAlO should be –3.69 kcal mol^{-1}, which is in agreement with the BAC-G2 value but is again more negative.[43]

Another example of an application of a composite method to the prediction of aluminum thermochemistry is that of Curtiss et al., who used the G3 method[9] (which corrects some of the deficiencies of the G2 method) to predict heats of formation for AlF_3 and $AlCl_3$. The G3 prediction for AlF_3 is in somewhat better agreement with the value in the *JANAF Tables* (1.1 kcal mol^{-1} deviation for G3 vs. –1.4 kcal mol^{-1} for G2), but the agreement is actually worse for $AlCl_3$, being 3.3 kcal mol^{-1} higher than the experimental value.

SC also report heats of formation obtained from DFT(B3LYP) calculations, and there is one application of a relatively new DFT variant, K2-BVWN, to $AlCl_3$. In all cases, the predictions of the DFT methods are high relative to both experiment and the BAC-G2 results, in some cases by large amounts. Predicted values for the hydrides are in generally good agreement with experiment, although in this case the prediction for AlH_2 is somewhat low with respect to the estimation of Gurvich et al., but within the estimated uncertainty. Agreement with the experimental values of the chlorides is poor in all three cases. For example, the DFT(B3LYP) prediction for $AlCl_3$ is too high by 13 kcal mol^{-1}. The K2-BVWN method is somewhat better, but is still > 5 kcal mol^{-1} higher than the experimental value.

As might be expected, the accuracy of the semiempirical approaches is poorer than that of the higher-level calculations, although this is not uniformly true. For example, in a recent paper, Thiel and Voityuk[30] described predictions for a small set of aluminum compounds obtained from AM1, PM3, MNDO, and a modified version of MDNO they developed that includes d orbitals (MNDO/d). Although most of these methods are reasonably accurate for closed-shell systems, errors can be high for both closed- and open-shell species. For example, MNDO/d predicts –149.2 kcal mol^{-1} for the heat of formation of $AlCl_3$, which is nearly 10 kcal mol^{-1} more negative than the established experimental result published by Gurvich et al. and in the *JANAF Tables.* With the exception of MNDO/d, the semiempirical methods disagree with the established heat of formation for AlCl by at least 6.5 kcal mol^{-1}. Although heats of formation for organometallic compounds are not as well established, the semiempirical predictions for $Al(CH_3)_3$ cover a range spanning nearly 35 kcal mol^{-1}. It would thus appear that these methods, in spite of their computational efficiency, are not sufficiently accurate to provide thermochemical data for modeling purposes.

IV. Summary and Conclusions

Thermodynamic data, in the form of heats of formation, entropies, and heat capacities, have been obtained from BAC-G2 predictions for a large set of aluminum compounds. In those cases where accurate experimental heats of formation are available (primarily halides), the BAC-G2 heat of formation is generally within 2 kcal mol^{-1} of the value reported in critical reviews. The good agreement between theory and experiment is particularly encouraging for compounds such as $AlCl_3$ that contain more than one halogen atom, the values predicted by G2 and other composite methods such as CBS and G3 deviate from experiment by $\geq$ 3 kcal mol^{-1} for $AlCl_3$. Predictions for organometallic compounds, though not firmly validated due to the lack of experimental data, appear well behaved. Similarly, data for hydroxides and other oxygen-

containing species are likely to be more accurate than either the limited experimental data available or the estimated values obtained from linear approximation methods.

Acknowledgements

This work was supported by the U.S. Department of Energy Office of Industrial Technologies, Pilkington North America, Inc. (Toledo, OH), and the NSF under grant CTS-9905265 (Dr. Farley Fisher, Program Director).

References

(1) Chase, M. W. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9*.
(2) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*; CRC Press: Boca Raton, 1994; Vol. 3.
(3) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11, Suppl. 2*.
(4) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970.
(5) Melius, C. F.; Allendorf, M. D.; Colvin, M. E. *Fourteenth Int. Symp. Chem. Vapor Deposition*, 1997, 97-25, 1.
(6) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
(7) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.
(8) Melius, C. F.; Allendorf, M. D. *J. Phys. Chem.* **2000**, *104*, 2168.
(9) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
(10) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570.
(11) Swihart, M. T.; Catoire, L. *Combust. Flame* **2000**, *121*, 210.
(12) Allendorf, M. D.; Melius, C. F. *Fundamental Gas-Phase and Surface Chemistry of Vapor Deposition Processes*, 1999, The Electrochemical Society Proceedings Series, PV98-23, 28.
(13) Allendorf, M. D.; Melius, C. F.; Bauschlicher Jr., C. *J. Phys. Fr. IV* **1999**, *9*, 8-23.
(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; T. Keith; Petersson, G. A.; Montgomery, J. A.; K. Raghavachari; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; J. B. Foresman; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; M. Challacombe; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.3*; Gaussian, Inc.: Pittsburgh, 1995.
(15) Melius, C. F. In *Chemistry and Physics of Energetic Materials*; Bulusu, S. N., Ed.; Kluwer Academic Publishers: Dorderecht, 1990; Vol. 309; pp 21.
(16) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120.
(17) Kee, R. J.; Rupley, F. M.; Miller, J. A.; Coltrin, M. E.; Grcar, J. F.; Meeks, E.; Moffat, H. K.; Lutz, A. E.; Dixon-Lewis, G.; Smooke, M. D.; Warnatz, J.; Evans, G. H.; Larson, R. S.; Mitchell, R. E.; Petzold, L. R.; Reynolds, W. C.; Caracotsios, M.; Stewart, W. E.; Glarborg, P.; Wang, C.; Adignun, O. Chemkin Collection; Release 3.6 ed.; Reaction Design, Inc.: San Diego, CA, 2000.
(18) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1992**, *96*, 428.
(19) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1993**, *97*, 720.
(20) Allendorf, M. D.; Melius, C. F.; Ho, P.; Zachariah, M. R. **1995**.
(21) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem. A* **1997**, *101*, 2670.
(22) Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1985**, *89*, 4647.
(23) Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1986**, *90*, 3399.

(24) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1995**, *99*, 2166.
(25) Melius, C. F.; Ho, P. *J. Phys. Chem.* **1991**, *95*, 1410-1419.
(26) Schwerdtfeger, P.; Heath, G. A.; Dolg, M.; Bennett, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 7518.
(27) Gutsev, G. L.; Jena, P. *J. Chem. Phys.* **1999**, *110*, 2928.
(28) Wong, M. W.; Radom, L. *J. Phys. Chem.* **1990**, *94*, 638.
(29) Bauschlicher Jr., C.; Langhoff, S. R.; Pettersson, L. G. M. *J. Chem. Phys.* **1988**, *89*, 5747.
(30) Thiel, W.; Voityuk, A. A. *J. Phys. Chem.* **1996**, *100*, 616 and references therein.
(31) Kafafi, S. A. *J. Phys. Chem. A* **1998**, *102*, 10404.
(32) Konings, R. J. M.; Booij, A. S. *J. Chem. Thermodynamics* **1992**, *24*, 1181.
(33) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 43.
(34) Smith, M. B. *J. Organomet. Chem.* **1974**, *76*, 171.
(35) Politzer, P.; Lane, P.; Grice, M. E. *J. Phys. Chem. A* **2001**, *105*, 7473.
(36) Barron, A. R. CVD of Insulating Materials. In *CVD of Nonmetals*; Rees Jr., W. S., Ed.; VCH: Weinheim, 1996; pp 262.
(37) Fredriksson, E.; Carlsson, J.-O. *J. Chem. Vapor Dep.* **1993**, *1*, 333.
(38) Long, L. H.; Norrish, R. G. W. *Phil. Trans. Roy. Soc. London* **1949**, *A241*, 587.
(39) Willis, B. G.; Jensen, K. F. *J. Phys. Chem. A* **2000**, *104*, 7881.
(40) Simka, H.; Willis, B. G.; Lengyel, I.; Jensen, K. F. *Prog. Crystal Growth Charact.* **1997**, *35*, 117.
(41) Edwards, A. H.; Jones, K. A. *J. Chem. Phys.* **1991**, *94*, 2894.
(42) Petrie, S. *J. Phys. Chem. A* **1998**, *102*, 7828.
(43) Swihart, M. T., personal commmunication, 2001.

Appendix

Table S7: Atomic Coordinates (Angstroms).

	Atom Number	Atomic Number	X	Y	Z
AlH_3					
	1	1	0.000000	0.000000	-1.588819
	2	13	0.000000	0.000000	0.000000
	3	1	1.375958	0.000000	0.794410
	4	1	-1.375958	0.000000	0.794410
AlH_2					
	1	1	-0.070825	0.000000	-1.545572
	2	13	-0.094790	0.000000	0.054727
	3	1	1.303093	0.000000	0.834122
AlH					
	1	13	0.000000	0.000000	-0.118488
	2	1	0.000000	0.000000	1.540338
$AlCl_3$					
	1	17	0.000000	2.069244	0.000000
	2	13	0.000000	0.000000	0.000000
	3	17	-1.792018	-1.034622	0.000000
	4	17	1.792018	-1.034622	0.000000
$AlCl_2\ ^2A_1$					
	1	17	0.000000	1.804187	-0.295438
	2	13	0.000000	0.000000	0.772684
	3	17	0.000000	-1.804187	-0.295438
$AlCl\ ^1\Sigma$					
	1	13	0.000000	0.000000	-1.209794
	2	17	0.000000	0.000000	0.925136
AlF_3					
	1	13	0.000000	0.000000	0.000000
	2	9	0.000000	0.000000	1.644717
	3	9	1.424367	0.000000	-0.822359
	4	9	-1.424367	0.000000	-0.822359
$AlF_2\ ^2A'$					
	1	9	0.000000	1.412270	-0.409309
	2	13	0.000000	0.018769	0.491318
	3	9	0.000000	-1.439381	-0.300372
$AlF\ ^1\Sigma$					
	1	13	0.000000	0.000000	-0.683459
	2	9	0.000000	0.000000	0.987218

	Atom Number	Atomic Number	X	Y	Z
$Al(OH)_3$ C_3 axis					
	1	13	0.000000	0.000000	0.000000
	2	8	-0.008305	0.000000	1.712172
	3	8	1.486937	0.000000	-0.848894
	4	8	-1.478632	0.000000	-0.863278
	5	1	0.828950	0.000000	2.196196
	6	1	1.487487	0.000000	-1.815990
	7	1	-2.316437	0.000000	-0.380207
$Al(OH)_2$ $^2A_1$ planar, trans, trans					
	1	13	0.000000	0.000000	0.494187
	2	8	0.000000	1.464544	-0.409032
	3	8	0.000000	-1.464544	-0.409032
	4	1	0.000000	2.310929	0.060046
	5	1	0.000000	-2.310929	0.060046
AlOH ^{1}A' linear					
	1	13	-0.244275	0.000000	-0.692842
	2	8	0.316342	0.000000	0.900642
	3	1	0.644840	0.000000	1.801804
$Al(CH_3)_3$					
	1	6	-0.721883	1.832006	-0.006156
	2	13	-0.000001	0.000002	0.000000
	3	6	-1.225624	-1.541180	0.000931
	4	6	1.947507	-0.290828	0.005227
	5	1	-1.358324	2.003446	-0.882131
	6	1	-1.359412	2.008818	0.867975
	7	1	0.053165	2.603545	-0.008005
	8	1	-1.058471	-2.178978	0.876746
	9	1	-1.057380	-2.180799	-0.873368
	10	1	-2.281322	-1.255747	-0.000070
	11	1	2.414736	0.175699	0.880355
	12	1	2.418860	0.171809	-0.869752
	13	1	2.228153	-1.347805	0.008243
$Al(CH_3)_2$ ^{2}A'					
	1	13	-0.497897	-0.257224	-0.287461
	2	6	-0.549253	0.155507	1.646484
	3	6	1.151270	0.155507	-1.298909
	4	1	-0.372699	1.224763	1.812687
	5	1	0.249589	-0.381041	2.171909
	6	1	-1.496283	-0.104810	2.123359
	7	1	1.383483	1.224763	-1.229110
	8	1	1.090741	-0.104810	-2.357499
	9	1	2.005723	-0.381041	-0.869805

	Atom Number	Atomic Number	X	Y	Z
$AlCH_3$ $^1A_1$					
	1	13	0.000000	0.000000	-0.871689
	2	6	0.000000	0.000000	1.122112
	3	1	1.018285	0.000000	1.533093
	4	1	-0.509142	0.881861	1.533093
	5	1	-0.509142	-0.881861	1.533093
AlH_2Cl					
	1	1	1.828389	0.856941	-1.055621
	2	13	0.462560	0.925120	-0.267059
	3	1	-0.271489	2.256859	0.156744
	4	17	-0.445305	-0.890609	0.257097
$AlHCl_2$					
	1	1	0.000000	0.000000	2.289292
	2	13	0.000000	0.000000	0.721237
	3	17	0.000000	1.788778	-0.343099
	4	17	0.000000	-1.788778	-0.343099
$HAlCl$ $^2A'$					
	1	1	-1.391012	1.835776	0.000000
	2	13	0.046644	1.133795	0.000000
	3	17	0.046155	-0.975006	0.000000
AlH_2F					
	1	13	0.000000	0.000000	-0.562981
	2	9	0.000000	0.000000	1.099735
	3	1	1.403103	0.000000	-1.289432
	4	1	-1.403103	0.000000	-1.289432
$AlHF_2$					
	1	13	0.000000	0.000000	0.433285
	2	1	0.000000	0.000000	1.998117
	3	9	1.413303	0.000000	-0.423935
	4	9	-1.413303	0.000000	-0.423935
HAlF					
	1	13	-0.080479	0.000000	-0.619190
	2	9	-0.032209	0.000000	1.047292
	3	1	1.336112	0.000000	-1.376163
H_2AlOH					
	1	8	0.046017	0.000000	-1.116225
	2	13	-0.075415	0.000000	0.599883
	3	1	0.913398	0.000000	-1.545040
	4	1	-1.542667	0.000000	1.186535
	5	1	1.241528	0.000000	1.489818

	Atom Number	Atomic Number	X	Y	Z
$HAl(OH)_2$ OAlOH cis, trans					
	1	13	0.017135	0.000000	0.463113
	2	1	0.061011	0.000000	2.039308
	3	8	1.503055	0.000000	-0.388645
	4	8	-1.439645	0.000000	-0.447574
	5	1	1.512500	0.000000	-1.356200
	6	1	-2.303551	0.000000	-0.013826
HAlOH ^{2}A' trans					
	1	13	-0.040286	0.000000	-0.666215
	2	8	-0.004594	0.000000	1.059733
	3	1	1.397835	0.000000	-1.370510
	4	1	-0.837368	0.000000	1.553438
$AlH_2(CH_3)$ HCAlH planar					
	1	13	0.003174	0.000000	-0.718084
	2	6	0.003585	0.000000	1.242945
	3	1	1.361082	0.000000	-1.552463
	4	1	-1.378878	0.000000	-1.512486
	5	1	1.007888	0.000000	1.672604
	6	1	-0.526432	0.875031	1.634882
	7	1	-0.526432	-0.875031	1.634882
$AlH(CH_3)_2$					
	1	1	0.000000	0.483176	-2.048823
	2	13	0.000000	0.116033	-0.492011
	3	6	1.730696	-0.097331	0.412714
	4	6	-1.730696	-0.097331	0.412714
	5	1	2.326393	0.819400	0.337465
	6	1	2.326357	-0.883897	-0.064167
	7	1	1.642066	-0.347319	1.472903
	8	1	-2.326393	0.819400	0.337465
	9	1	-1.642066	-0.347319	1.472903
	10	1	-2.326357	-0.883897	-0.064167
$HAl(CH_3)$ ^{2}A' HAlCH trans					
	1	13	0.365350	-0.350440	0.611196
	2	1	0.325463	-1.956178	0.544469
	3	6	-0.503472	0.662592	-0.842261
	4	1	-0.434187	1.745444	-0.726354
	5	1	-1.564708	0.395449	-0.903911
	6	1	-0.055286	0.395449	-1.806187
$AlFCl_2$					
	1	13	0.000000	0.000000	0.350858
	2	9	0.000000	0.000000	1.998363
	3	17	1.799331	0.000000	-0.663130
	4	17	-1.799331	0.000000	-0.663130

	Atom Number	Atomic Number	X	Y	Z
AlF_2Cl					
	1	13	0.000000	0.000000	-0.415425
	2	17	0.000000	0.000000	1.646789
	3	9	1.415890	0.000000	-1.255271
	4	9	-1.415890	0.000000	-1.255271
ClAlF					
	1	13	-0.798777	0.000000	0.069247
	2	9	-0.779176	0.000000	1.728533
	3	17	1.023335	0.000000	-0.968059
$Al(OH)Cl_2$					
	1	8	-0.127190	2.044509	-0.008033
	2	13	-0.025316	0.347011	-0.001599
	3	1	-0.974061	2.510356	-0.061517
	4	17	1.852555	-0.515395	0.116999
	5	17	-1.716044	-0.859756	-0.108378
$AlCl(OH)_2$ OAlOH cis, trans					
	1	13	0.000226	0.000000	-0.407029
	2	17	0.035008	0.000000	1.674885
	3	8	1.491903	0.000000	-1.231211
	4	8	-1.464083	0.000000	-1.285504
	5	1	1.506342	0.000000	-2.199096
	6	1	-2.326982	0.000000	-0.848842
ClAlOH ^{2}A', trans					
	1	13	-0.793530	0.000000	0.047046
	2	8	-0.703024	0.000000	1.761798
	3	17	1.026604	0.000000	-1.000021
	4	1	-1.512190	0.000000	2.294362
$AlCl_2(CH_3)$ HCAlCl planar					
	1	13	0.007122	0.000000	0.334418
	2	6	0.003877	0.000000	2.272864
	3	17	1.775467	0.000000	-0.779530
	4	17	-1.780642	0.000000	-0.748899
	5	1	1.015990	0.000000	2.682821
	6	1	-0.521932	0.878804	2.657932
	7	1	-0.521932	-0.878804	2.657932

	Atom Number	Atomic Number	X	Y	Z
$AlCl(CH_3)_2$					
	1	17	-1.677844	0.066598	-0.330975
	2	13	0.395303	-0.015690	0.077978
	3	6	1.245083	-1.764539	-0.099501
	4	6	1.245083	1.665698	0.590717
	5	1	1.126547	-2.156404	-1.114852
	6	1	0.780678	-2.495477	0.570276
	7	1	2.314477	-1.736417	0.125648
	8	1	1.126547	2.419776	-0.194051
	9	1	2.314477	1.552684	0.787468
	10	1	0.780678	2.080700	1.491077
$AlCl(CH_3)$ trans					
	1	13	-0.610727	-0.549583	0.097588
	2	17	0.409370	1.162676	0.813633
	3	6	0.060786	-1.353420	-1.568088
	4	1	1.106388	-1.653110	-1.442767
	5	1	0.025235	-0.617789	-2.378266
	6	1	-0.516178	-2.229493	-1.870847
$AlF_2(OH)$					
	1	8	0.019418	1.682944	0.000000
	2	13	0.011302	-0.016125	0.000000
	3	1	-0.803116	2.190985	0.000000
	4	9	1.446880	-0.825393	0.000000
	5	9	-1.391231	-0.890708	0.000000
$AlF(OH)_2$ FAlOH cis, cis					
	1	9	-0.000001	-1.657324	0.000000
	2	13	0.000000	0.004428	0.000000
	3	8	0.000001	0.876326	1.463539
	4	8	0.000001	0.876326	-1.463539
	5	1	0.000000	0.418568	2.314745
	6	1	0.000000	0.418568	-2.314745
FAlOH trans					
	1	13	-0.304861	0.388598	0.000000
	2	8	1.411720	0.453625	0.000000
	3	9	-1.020389	-1.110703	0.000000
	4	1	1.852931	1.315556	0.000000

	Atom Number	Atomic Number	X	Y	Z
$Al(OH)_2CH_3$ OAlOH cis, trans					
	1	13	-0.000070	-0.000135	-0.043144
	2	6	0.036858	-0.001432	1.904590
	3	8	1.478648	-0.160920	-0.903329
	4	8	-1.420331	0.152114	-1.007944
	5	1	1.466179	-0.160604	-1.871116
	6	1	-2.298025	0.247327	-0.614809
	7	1	-0.358621	0.929867	2.320798
	8	1	1.061985	-0.117746	2.264725
	9	1	-0.558294	-0.818045	2.323918
$Al(OH)(CH_3)_2$					
	1	8	-0.222706	0.547845	0.535121
	2	13	-0.073754	0.040921	2.181475
	3	6	1.687395	-0.277925	2.988507
	4	6	-1.761082	-0.183696	3.142719
	5	1	2.524560	0.071113	2.377449
	6	1	1.840181	-1.348481	3.165868
	7	1	1.764798	0.212025	3.964837
	8	1	-2.614733	-0.158002	2.460700
	9	1	-1.905779	0.614583	3.878821
	10	1	-1.797926	-1.127961	3.695144
	11	1	0.559046	0.700593	-0.013734
CH_3AlOH HOAlC cis					
	1	6	-0.447374	0.012178	-1.616326
	2	13	-0.452855	-0.054840	0.360382
	3	8	1.011373	0.051468	1.275705
	4	1	1.869912	0.137167	0.833779
	5	1	0.558688	-0.054363	-2.041626
	6	1	-1.048856	-0.804017	-2.027170
	7	1	-0.899367	0.949316	-1.957624
HAl(OH)Cl ClAlOH cis					
	1	8	-0.750592	0.000000	-1.779584
	2	13	-0.755119	0.000000	-0.072173
	3	1	0.063084	0.000000	-2.303298
	4	1	-2.130126	0.000000	0.681497
	5	17	1.052254	0.000000	0.988042
$HAl(CH_3)Cl$ HCAlCl trans					
	1	13	-0.755956	0.000000	-0.003709
	2	6	-0.714297	0.000000	1.943977
	3	17	1.074101	0.000000	-1.043919
	4	1	-2.060411	0.000000	-0.900420
	5	1	-1.718807	0.000000	2.375189
	6	1	-0.183644	-0.876894	2.328105
	7	1	-0.183644	0.876894	2.328105

	Atom Number	Atomic Number	X	Y	Z
$HAl(OH)CH_3$ CAlOH trans, HCAlO cis					
	1	13	-0.380269	0.083460	-0.302596
	2	6	-0.391041	0.020768	1.645965
	3	8	1.124550	-0.180424	-1.102570
	4	1	-1.674414	0.362822	-1.191300
	5	1	1.174089	-0.157865	-2.068597
	6	1	-0.737828	0.968062	2.071861
	7	1	0.602326	-0.184756	2.051936
	8	1	-1.070833	-0.754468	2.014614
$Al(OH)CH_3Cl$					
	1	13	0.094228	0.036285	-0.055494
	2	6	0.059233	0.004107	1.882496
	3	8	1.568365	-0.179934	-0.899868
	4	17	-1.661756	0.335230	-1.177205
	5	1	1.615989	-0.168648	-1.866402
	6	1	-0.321751	0.946516	2.286302
	7	1	1.059559	-0.161662	2.289038
	8	1	-0.595768	-0.789867	2.252523
$AlO\ ^2\Sigma$					
	1	13	0.000000	0.000000	-0.627735
	2	8	0.000000	0.000000	1.020070
$HAlO\ ^1\Sigma$					
	1	8	0.000000	0.000000	-1.108153
	2	13	0.000000	0.000000	0.520868
	3	1	0.000000	0.000000	2.093938
$H_2AlO\ ^2B_2$					
	1	8	0.000000	0.000000	-1.206275
	2	13	0.000000	0.000000	0.551180
	3	1	1.420081	0.000000	1.242427
	4	1	-1.420081	0.000000	1.242427
$AlC\ ^4\Sigma^-$					
	1	13	0.000000	0.000000	-0.620877
	2	6	0.000000	0.000000	1.345233
AlCH singlet linear					
	1	13	-0.270680	0.000000	-0.274469
	2	6	0.412127	0.000000	1.547509
	3	1	0.793861	0.000000	2.566960
HAlCH HAlCH trans $^2A''$					
	1	13	-0.082743	-0.092090	-0.619087
	2	6	0.057174	0.185732	1.237010
	3	1	1.198948	-0.253011	-1.550185
	4	1	-0.466329	0.335794	2.176256

	Atom Number	Atomic Number	X	Y	Z
$HAlCH_2$ singlet linear C_{2V}					
	1	13	0.000000	0.634320	0.000000
	2	1	0.000000	2.208762	0.000000
	3	6	0.000000	-1.160675	0.000000
	4	1	-0.916517	-1.745439	0.000000
	5	1	0.916517	-1.745439	0.000000
H_2AlCH $^3A"$					
	1	13	0.053764	0.000000	-0.577885
	2	6	-0.091933	0.000000	1.312216
	3	1	1.496400	0.000000	-1.237502
	4	1	-1.256560	0.000000	-1.474689
	5	1	-0.387168	0.000000	2.351400
AlH_2OCH_3 HCOAl cis					
	1	13	-0.465070	0.000000	-1.097101
	2	8	-0.261576	0.000000	0.604408
	3	6	0.925787	0.000000	1.379392
	4	1	0.822127	0.000000	-2.029049
	5	1	-1.956404	0.000000	-1.620246
	6	1	1.831733	0.000000	0.761038
	7	1	0.943171	0.886846	2.019480
	8	1	0.943171	-0.886846	2.019480

Table S8. Moments of Inertia (amu Bohr^2).

	I_1	I_2	I_3
AlH_3	13.628	13.628	27.255
AlH_2	4.513	13.587	18.101
AlH	0.000	9.547	9.547
$AlCl_3$	802.036	802.036	1604.071
$AlCl_2$ $^2A_1$	79.324	812.965	892.290
AlCl $^1\Sigma$	0.000	247.896	247.896
AlF_3	275.289	275.289	550.578
AlF_2 $^2A'$	40.400	276.256	316.655
AlF $^1\Sigma$	0.000	111.122	111.122
$Al(OH)_3$ C_3 axis	280.923	280.923	561.846
$Al(OH)_2$ $^2A_1$ planar, trans, trans	42.662	283.468	326.130
AlOH $^1A'$ linear	0.000	116.671	116.671
$Al(CH_3)_3$	365.770	365.771	698.471
$Al(CH_3)_2$ $^2A'$	76.512	351.553	405.788
$AlCH_3$ $^1A_1$	11.195	155.649	155.649
AlH_2Cl	14.106	264.591	278.697
$AlHCl_2$	98.202	799.139	897.341
HAlCl $^2A'$	6.946	254.917	261.863
AlH_2F	14.171	123.842	138.013
$AlHF_2$	56.531	271.029	327.560
HAlF	6.825	118.061	124.886
H_2AlOH	16.379	128.835	145.214
$HAl(OH)_2$ OAlOH cis, trans	62.288	274.798	337.086
HAlOH $^2A'$ trans	8.921	123.065	131.986
$AlH_2(CH_3)$ HCAlH planar	24.673	167.080	180.730
$AlH(CH_3)_2$	83.532	365.057	426.544
$HAl(CH_3)$ $^2A'$ HAlCH trans	17.901	160.393	167.164
$AlFCl_2$	392.587	808.595	1201.183
AlF_2Cl	272.022	569.025	841.047
ClAlF	52.176	501.412	553.588
$Al(OH)Cl_2$	394.091	807.907	1201.998
$AlCl(OH)_2$ OAlOH cis, trans	277.266	566.653	843.919
ClAlOH $^2A'$,trans	55.058	494.418	549.476
$AlCl_2(CH_3)$ HCAlCl planar	457.648	800.928	1247.457
$AlCl(CH_3)_2$	372.061	580.760	930.693
$AlCl(CH_3)$ trans	77.924	521.787	588.496
$AlF_2(OH)$	275.164	278.963	554.126
$AlF(OH)_2$ FAlOH cis, cis	275.065	283.259	558.323
FAlOH trans	41.475	279.738	321.214
$Al(OH)_2CH_3$ OAlOH cis, trans	280.801	336.577	606.238
$Al(OH)(CH_3)_2$	309.072	364.945	651.855
CH_3AlOH HOAlC cis	60.401	320.239	369.476
HAl(OH)Cl ClAlOH cis	73.187	492.088	565.275
$HAl(CH_3)Cl$ HCAlCl trans	91.393	523.893	604.216
$HAl(OH)CH_3$ CAlOH trans, HCAlO cis	73.641	315.104	377.655
$Al(OH)CH_3Cl$	315.736	586.512	891.122
AlO $^2\Sigma$	0.000	97.370	97.370

	I_1	I_2	I_3
HAlO $^1\Sigma$	0.000	111.865	111.865
H_2AlO $^2B_2$	14.516	123.205	137.720
AlC $^4\Sigma^-$	0.000	114.657	114.657
AlCH singlet linear	0.000	133.099	133.099
HAlCH HAlCH trans $^2A''$	6.650	131.042	137.692
$HAlCH_2$ singlet linear C_{2V}	6.046	135.681	141.727
H_2AlCH $^3A''$	13.876	140.242	154.118
AlH_2OCH_3 HCOAl cis	42.045	338.687	369.409

Table S9. Scaled Vibrational Frequencies (cm^{-1}).

Species	ν	ν	ν	ν	ν
AlH_3	678.5	755.6	755.6	1811.3	1811.3
	1815.5				
AlH_2	732.3	1743.0	1762.9		
AlH	1580.9				
$AlCl_3$	139.8	139.8	190.7	356.7	573.4
	573.4				
$AlCl_2$ $^2A_1$	145.2	428.8	524.7		
AlCl $^1\Sigma$	424.7				
AlF_3	242.3	242.3	282.2	665.6	923.8
	923.8				
AlF_2 $^2A'$	245.1	738.0	868.5		
AlF $^1\Sigma$	771.2				
$Al(OH)_3$ $_3$ axis	216.2	216.2	255.7	327.7	327.7
	334.3	603.2	621.6	621.6	657.7
	884.8	884.8	3729.1	3729.1	3731.1
$Al(OH)_2$ $^2A_1$ planar ,trans, trans	232.8	265.3	291.4	540.8	612.0
	711.8	856.5	3730.4	3730.7	
AlOH $^1A'$ linear	148.5	781.5	3780.6		
$Al(CH_3)_3$	22.7	22.8	38.8	157.3	157.3
	175.1	473.1	553.9	553.9	575.9
	596.1	596.1	708.0	736.6	736.6
	1246.6	1246.6	1250.6	1428.4	1428.4
	1429.1	1431.3	1431.3	1432.5	2822.7
	2822.7	2824.7	2868.4	2868.4	2869.0
	2893.5	2894.4	2894.4		
$Al(CH_3)_2$ $^2A'$	27.0	44.0	157.2	512.5	536.1
	553.0	559.5	630.2	732.5	1228.7
	1236.8	1419.6	1424.6	1426.8	1435.4
	2820.3	2822.7	2869.7	2871.7	2907.1
	2907.3				
$AlCH_3$ $^1A_1$	482.8	482.8	530.8	1228.9	1414.9
	1414.9	2797.6	2854.9	2854.9	
AlH_2Cl	479.1	490.3	579.7	746.7	1853.5
	1861.3				
$AlHCl_2$	154.4	433.3	443.6	539.4	634.4
	1899.6				
HAlCl $^2A'$	461.2	551.6	1750.6		
AlH_2F	547.7	607.5	747.9	816.9	1851.6
	1851.6				
$AlHF_2$	261.3	481.1	654.6	751.4	893.6
	1908.8				
HAlF	584.3	789.2	1717.4		
H_2AlOH	399.3	470.7	602.7	653.9	741.8
	812.8	1812.7	1843.6	3727.1	
$HAl(OH)_2$ OAlOH cis, trans	228.6	309.8	359.8	495.8	543.6
	613.6	679.6	745.9	870.6	1857.7
	3724.7	3734.8			

Species	ν	ν	ν	ν	ν
HAlOH $^2A'$ trans	396.0	526.0	646.9	776.8	1733.7
	3727.3				
$AlH_2(CH_3)$ HCAlH planar	14.0	391.0	465.7	576.5	698.5
	736.5	768.7	1248.7	1427.4	1430.6
	1788.7	1795.9	2829.9	2877.4	2906.1
$AlH(CH_3)_2$	19.9	29.8	167.5	367.0	498.0
	516.5	549.6	619.3	705.7	730.6
	759.3	1246.6	1249.5	1424.7	1429.0
	1431.0	1432.3	1771.1	2826.2	2827.1
	2872.8	2873.6	2899.0	2900.5	
$HAl(CH_3)$ $^2A'$ HAlCH trans	85.7	444.9	547.9	568.4	739.7
	1232.8	1421.5	1430.3	1724.7	2825.5
	2875.9	2913.2			
$AlFCl_2$	144.4	196.1	220.3	405.5	581.7
	854.1				
AlF_2Cl	178.0	229.9	251.3	471.8	792.9
	914.9				
ClAlF	189.9	468.4	812.8		
$Al(OH)Cl_2$	145.1	185.6	216.2	326.4	403.9
	534.4	607.1	852.2	3730.4	
$AlCl(OH)_2$ OAlOH cis, trans	174.2	207.1	238.7	321.6	330.4
	450.6	590.9	608.4	777.2	896.6
	3725.7	3735.7			
ClAlOH $^2A'$ trans	186.6	296.7	453.9	566.0	803.5
	3727.0				
$AlCl_2(CH_3)$ HCAlCl planar	9.5	145.2	148.5	181.1	386.8
	525.2	638.2	662.5	711.0	1253.9
	1423.4	1425.1	2846.2	2902.8	2924.4
$AlCl(CH_3)_2$	26.6	33.7	152.8	153.2	178.0
	413.1	551.6	574.1	622.6	673.6
	692.0	737.4	1250.7	1254.0	1422.9
	1425.7	1429.3	1429.3	2836.1	2837.7
	2891.0	2891.6	2903.6	2905.1	
$AlCl(CH_3)$ trans	47.6	151.9	432.9	574.8	574.9
	681.8	1225.0	1418.1	1424.9	2837.0
	2896.6	2918.2			
$AlF_2(OH)$	225.1	246.4	277.0	323.4	575.0
	665.6	899.9	921.7	3738.6	
$AlF(OH)_2$ FAlOH cis, cis	226.0	227.5	269.6	279.9	333.1
	567.6	598.2	666.6	875.5	915.0
	3738.5	3739.6			
FAlOH trans	239.7	299.7	572.1	724.6	864.9
	3728.2				
$Al(OH)_2CH_3$ OAlOH cis, trans	8.9	174.3	221.1	224.1	304.6
	367.1	536.0	574.8	625.9	661.5
	684.0	779.4	861.7	1251.4	1432.7
	1434.6	2838.6	2889.9	2911.6	3722.4
	3736.7				

Species	ν	ν	ν	ν	ν
$Al(OH)(CH_3)_2$	16.5	24.8	156.3	194.6	201.9
	351.1	500.8	568.3	580.8	596.6
	683.9	694.9	700.7	814.8	1247.9
	1250.7	1429.3	1430.0	1432.7	1433.8
	2825.6	2831.2	2878.1	2880.4	2894.2
	2905.9	3730.0			
CH_3AlOH	10.0	172.7	321.4	515.2	559.7
HOAlC cis	575.9	676.2	760.1	1222.4	1423.4
	1431.5	2806.5	2881.6	2908.1	3683.3
HAl(OH)Cl	191.3	356.8	463.2	464.5	578.8
ClAlOH cis	657.1	824.6	1893.9	3730.8	
$HAl(CH_3)Cl$	17.9	158.3	378.8	449.9	574.7
HCAlCl trans	619.7	669.8	738.5	1252.6	1425.0
	1426.4	1841.6	2838.8	2894.5	2907.3
$HAl(OH)CH_3$	32.0	192.3	327.6	449.4	522.3
CAlOH trans, HCAlO cis	565.0	670.8	678.5	720.4	820.2
	1248.4	1428.8	1430.6	1793.2	2833.5
	2882.1	2910.7	3727.8		
$Al(OH)CH_3Cl$	30.8	148.6	190.9	199.1	360.3
	424.6	583.0	619.4	666.4	706.8
	833.1	1252.2	1427.6	1428.1	2845.8
	2902.1	2919.1	3729.8		
AlO $^2\Sigma$	722.1				
HAlO $^1\Sigma$	432.6	432.6	1069.2	1914.6	
H_2AlO $^2B_2$	461.2	586.5	691.9	775.4	1849.2
	1855.3				
AlC $^4\Sigma^-$	595.3				
AlCH singlet linear	499.4	640.0	3023.5		
HAlCH	365.3	441.3	566.7	676.3	1768.8
$^2A''$ HAlCH trans	3006.3				
$HAlCH_2$	120.5	358.1	605.1	655.8	841.5
singlet linear C_{2V}	1338.1	1884.3	2945.0	3014.2	
H_2AlCH $^3A''$	123.7	299.2	490.7	576.2	680.8
	767.3	1811.5	1819.6	3041.6	
AlH_2OCH_3	83.2	147.6	174.2	539.7	599.9
HCOAl cis	661.6	766.4	1139.6	1167.8	1189.4
	1469.6	1478.0	1484.7	1811.4	1840.6
	2840.7	2892.2	2907.0		

Table S10: Calculated Electronic Energies for Al-H-C-O-F-Cl Compounds at G2 Level of Theory (hartrees).

Species	G2
AlH_3	-243.753958
AlH_2	-243.118964
AlH	-242.546190
$AlCl_3$	-1621.448747
$AlCl_2$ $^2A_1$	-1161.585244
AlCl $^1\Sigma$	-701.800168
AlF_3	-541.499452
AlF_2 $^2A'$	-441.618733
AlF $^1\Sigma$	-341.821260
$Al(OH)_3$ C_3 axis	-469.400344
$Al(OH)_2$ $^2A_1$ planar,trans,trans	-393.548819
AlOH $^1A'$ linear	-317.784010
$Al(CH_3)_3$	-361.476928
$Al(CH_3)_2$ $^2A'$	-321.599290
$AlCH_3$ $^1A_1$	-281.789132
AlH_2Cl	-702.987801
$AlHCl_2$	-1162.220232
HAlCl $^2A'$	-702.353344
AlH_2F	-343.005223
$AlHF_2$	-442.256099
HAlF	-342.369944
H_2AlOH	-318.970018
$HAl(OH)_2$ OAlOH cis,trans	-394.186773
HAlOH $^2A'$ trans	-318.334669
$AlH_2(CH_3)$ HCAlH planar	-282.994635
$AlH(CH_3)_2$	-322.235711
$HAl(CH_3)$ $^2A'$ HAlCH trans	-282.358735
$AlFCl_2$	-1261.465704
AlF_2Cl	-901.482694
ClAlF	-801.601716
$Al(OH)Cl_2$	-1237.433798
$AlCl(OH)_2$ OAlOH cis, trans	-853.417789
ClAlOH $^2A'$,trans	-777.567650
$AlCl_2(CH_3)$ HCAlCl planar	-1201.464929
$AlCl(CH_3)_2$	-781.473995
$AlCl(CH_3)$ trans	-741.595938
$AlF_2(OH)$	-517.467592
$AlF(OH)_2$ FAlOH cis, cis	-493.434284
FAlOH trans	-417.584276
$Al(OH)_2CH_3$ OAlOH cis, trans	-433.429104
$Al(OH)(CH_3)_2$	-397.454003
CH_3AlOH HAOLC cis	-357.574221
HAl(OH)Cl ClAlOH cis	-778.204910
$HAl(CH_3)Cl$ HCAlCl trans	-742.231008
$HAl(OH)CH_3$ CAlOH trans,hcalo cis	-358.212373
$Al(OH)CH_3Cl$	-817.448704

Species	G2
AlO $^2\Sigma$	-317.102389
HAlO $^1\Sigma$	-317.717402
H_2AlO $^2B_2$	-318.278195
AlC $^4\Sigma^-$	-279.837286
AlCH singlet linear	-280.443388
HAlCH HAlCH trans $^2A''$	-281.076878
$HAlCH_2$ singlet linear C_{2V}	-281.730266
H_2AlCH $^3A''$	-281.681210
AlH_2OCH_3 HCOAl cis	-358.173936
Al	-241.930950
H	-0.500000
Cl	-459.676627
F	-99.632814
O	-74.982030
C	-37.784301

Table S11. Polynomial Coefficients for Thermochemical Data in CHEMKIN[a] format.

```
AlH3                    H   3Al  1    0    0G   300.000  3000.000 1000.00    0 1
 0.36136173E+01 0.86060067E-02-0.49030616E-05 0.13093924E-08-0.13426153E-12    2
 0.14005457E+05 0.17496452E+01 0.25175901E+01 0.10497049E-01-0.51033191E-05    3
 0.42088884E-09 0.15948427E-12 0.14386092E+05 0.77525506E+01                   4

AlH2                    H   2Al  1    0    0G   300.000  3000.000 1000.00    0 1
 0.32629111E+01 0.50466104E-02-0.28814143E-05 0.77111851E-09-0.79223387E-13    2
 0.31055749E+05 0.56251145E+01 0.37869097E+01 0.72466810E-03 0.66452812E-05    3
-0.74124397E-08 0.23755831E-11 0.31072085E+05 0.36782064E+01                   4

AlH                     H   1Al  1    0    0G   300.000  3000.000 1000.00    0 1
 0.29913047E+01 0.20894600E-02-0.12165514E-05 0.33063586E-09-0.34391629E-13    2
 0.28827046E+05 0.49311859E+01 0.36951400E+01-0.23219920E-02 0.79194099E-05    3
-0.75222719E-08 0.23901715E-11 0.28761931E+05 0.19242302E+01                   4

AlCl3                   Al  1Cl  3    0    0G   300.000  3000.000 1000.00    0 1
 0.93315504E+01 0.94087032E-03-0.54168101E-06 0.14379077E-09-0.14532189E-13    2
-0.74135693E+05-0.15788797E+02 0.53258550E+01 0.19081379E-01-0.32420784E-04    3
 0.25503251E-07-0.76297036E-11-0.73390715E+05 0.31312484E+01                   4

AlCl2 2A1               Al  1Cl  2    0    0G   300.000  3000.000 1000.00    0 1
 0.66317414E+01 0.51378823E-03-0.29294840E-06 0.77014564E-10-0.77103876E-14    2
-0.28423278E+05-0.31849167E+01 0.42237259E+01 0.11497745E-01-0.19714373E-04    3
 0.15600056E-07-0.46852682E-11-0.27978681E+05 0.81708628E+01                   4

AlCl 1sigma             Al  1Cl  1    0    0G   300.000  3000.000 1000.00    0 1
 0.43650488E+01 0.18564461E-03-0.10411274E-06 0.26913038E-10-0.26495484E-14    2
-0.73226583E+04 0.24702735E+01 0.33720458E+01 0.47578656E-02-0.82539209E-05    3
 0.65818785E-08-0.19870248E-11-0.71410293E+04 0.71434838E+01                   4

AlF3                    F   3Al  1    0    0G   300.000  3000.000 1000.00    0 1
 0.80899255E+01 0.28084728E-02-0.16933344E-05 0.46998815E-09-0.49519149E-13    2
-0.14721820E+06-0.13832194E+02 0.31369899E+01 0.23030198E-01-0.34000791E-04    3
 0.24231467E-07-0.67723314E-11-0.14620279E+06 0.10073686E+02                   4

AlF2 2A'          111601F   2Al  1    0    0G   300.000  3000.000 1000.00    0 1
  0.58773701E+01 0.16568770E-02-0.10016144E-05 0.27854896E-09-0.29393794E-13    2
 -0.76890498E+05-0.23171139E+01 0.28563439E+01 0.13990770E-01-0.20675507E-04    3
  0.14708760E-07-0.40985789E-11-0.76272170E+05 0.12261675E+02                   4

AlF 1sigma              F   1Al  1    0    0G   300.000  3000.000 1000.00    0 1
 0.40033527E+01 0.73539741E-03-0.44555701E-06 0.12412623E-09-0.13116773E-13    2
-0.32882780E+05 0.27481167E+01 0.26458597E+01 0.62664647E-02-0.92398742E-05    3
 0.65495308E-08-0.18177784E-11-0.32604800E+05 0.93008017E+01                   4

Al(OH)3 C3 axis    72401H   3O   3Al  1    0G   300.000  3000.000 1000.00    0 1
 0.14727820E+02-0.66992604E-03 0.18330674E-05-0.72963835E-09 0.91011438E-13    2
-0.12225153E+06-0.47178942E+02-0.29820043E-02 0.68547616E-01-0.12026094E-03    3
 0.94728953E-07-0.27760315E-10-0.11972588E+06 0.21550595E+02                   4

Al(OH)2 2A1 planar      H   2O   2Al  1    0G   300.000  3000.000 1000.00    0 1
 0.96518823E+01-0.68692424E-04 0.11357681E-05-0.49010375E-09 0.63207907E-13    2
-0.58997622E+05-0.20709573E+02 0.26094049E+01 0.35533525E-01-0.65323792E-04    3
 0.53792274E-07-0.16319350E-10-0.57897149E+05 0.11567214E+02                   4
```

```
AlOH 1A' linear         H   1O   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.52817396E+01 0.75726795E-03 0.75329534E-07-0.10248966E-09 0.15947418E-13    2
-0.23157811E+05-0.54226919E+01 0.39478484E+01 0.71903061E-02-0.11186529E-04    3
 0.84576790E-08-0.23815091E-11-0.22947036E+05 0.73536832E+00                   4

Al(CH3)3                H   9C   3Al  1    0G   300.000  3000.000 1000.00    0 1
 0.54565587E+01 0.33630084E-01-0.16636859E-04 0.39870175E-08-0.37587108E-12    2
-0.95254466E+04 0.92997488E+01 0.22248582E+01 0.48643936E-01-0.43865122E-04    3
 0.26328789E-07-0.72715314E-11-0.89308953E+04 0.24500482E+02                   4

Al(CH3)2 2A'            H   6C   2Al  1    0G   300.000  3000.000 1000.00    0 1
 0.42476118E+01 0.21997354E-01-0.10831479E-04 0.25851225E-08-0.24284556E-12    2
 0.16024834E+05 0.11422025E+02 0.23584282E+01 0.31114834E-01-0.27823370E-04    3
 0.16773201E-07-0.46673284E-11 0.16357119E+05 0.20227270E+02                   4

AlCH3 1A1               H   3C   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.33858389E+01 0.10689312E-01-0.52493455E-05 0.12489087E-08-0.11693916E-12    2
 0.20496741E+05 0.65398826E+01 0.28518820E+01 0.13815289E-01-0.11937265E-04    3
 0.73826468E-08-0.21547769E-11 0.20571149E+05 0.89111900E+01                   4

AlH2Cl                  H   2Al  1Cl  1    0G   300.000  3000.000 1000.00    0 1
 0.54797946E+01 0.60291321E-02-0.34011143E-05 0.90006488E-09-0.91540392E-13    2
-0.16142639E+05-0.26502271E+01 0.25710559E+01 0.17828258E-01-0.23054177E-04    3
 0.16443768E-07-0.48725681E-11-0.15512163E+05 0.11484056E+02                   4

AlHCl2                  H   1Al  1Cl  2    0G   300.000  3000.000 1000.00    0 1
 0.74012122E+01 0.34526363E-02-0.19350664E-05 0.50829419E-09-0.51304481E-13    2
-0.45787457E+05-0.85762363E+01 0.35817709E+01 0.20395813E-01-0.31659475E-04    3
 0.24405345E-07-0.73476829E-11-0.45046455E+05 0.95849675E+01                   4

HAlCl 2A'               H   1Al  1Cl  1    0G   300.000  3000.000 1000.00    0 1
 0.49516450E+01 0.27647135E-02-0.15722649E-05 0.41848253E-09-0.42741595E-13    2
 0.87852967E+03 0.19588845E+01 0.35225653E+01 0.84786291E-02-0.10970102E-04    3
 0.77887282E-08-0.22999863E-11 0.11921514E+04 0.89231827E+01                   4

AlH2F                   H   2F   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.50227364E+01 0.67336170E-02-0.38428006E-05 0.10266715E-08-0.10524188E-12    2
-0.40621323E+05-0.18200974E+01 0.17967045E+01 0.19003779E-01-0.22880150E-04    3
 0.15195011E-07-0.42803625E-11-0.39891650E+05 0.14034054E+02                   4

AlHF2                   H   1F   2Al  1    0G   300.000  3000.000 1000.00    0 1
 0.65502286E+01 0.47346363E-02-0.27271025E-05 0.73304033E-09-0.75449238E-13    2
-0.95116571E+05-0.71806890E+01 0.20887755E+01 0.23020337E-01-0.32488675E-04    3
 0.23244895E-07-0.66499794E-11-0.94190502E+05 0.14372703E+02                   4

HAlF                    H   1F   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.45841938E+01 0.33458489E-02-0.19421706E-05 0.52554425E-09-0.54404340E-13    2
-0.23293111E+05 0.23191574E+01 0.28234906E+01 0.96781098E-02-0.11097421E-04    3
 0.68820748E-08-0.18272424E-11-0.22881353E+05 0.11051394E+02                   4

H2AlOH                  H   3O   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.72973364E+01 0.57965725E-02-0.29222352E-05 0.72069375E-09-0.70071173E-13    2
-0.31766945E+05-0.13155804E+02 0.65214085E+00 0.33292168E-01-0.47346473E-04    3
 0.33663165E-07-0.94387043E-11-0.30423359E+05 0.18825438E+02                   4
```

```
HAl(OH)2 OAlOcis   72401H   3O   2Al  1    0G   300.000  3000.000 1000.00    0 1
 0.10901080E+02 0.26022129E-02-0.51732323E-06-0.22184311E-10 0.13144113E-13    2
-0.77484649E+05-0.28833360E+02 0.23691655E+00 0.51669211E-01-0.86322567E-04    3
 0.67043964E-07-0.19650595E-10-0.75586026E+05 0.21228249E+02                   4

HAlOH 2A' trans         H   2O   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.67873102E+01 0.22995619E-02-0.87374109E-06 0.16290839E-09-0.12069563E-13    2
-0.14486646E+05-0.91455541E+01 0.15271630E+01 0.25369749E-01-0.39663157E-04    3
 0.29571767E-07-0.84415525E-11-0.13498105E+05 0.15819194E+02                   4

AlH2(CH3)               H   5C   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.42179887E+01 0.16955440E-01-0.88170886E-05 0.22022709E-08-0.21479437E-12    2
 0.61598754E+04 0.64439127E+01 0.18131674E+01 0.25898396E-01-0.22676393E-04    3
 0.12711296E-07-0.34026497E-11 0.67233015E+04 0.18336481E+02                   4

AlH(CH3)2               H   7C   2Al  1    0G   300.000  3000.000 1000.00    0 1
 0.48344201E+01 0.25295015E-01-0.12727832E-04 0.30947810E-08-0.29533678E-12    2
-0.17097813E+04 0.76702702E+01 0.17170905E+01 0.38606215E-01-0.35570086E-04    3
 0.21315009E-07-0.58671805E-11-0.10746550E+04 0.22633500E+02                   4

HAl(CH3) 2A'            H   4C   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.37577924E+01 0.13516201E-01-0.68522145E-05 0.16767532E-08-0.16086964E-12    2
 0.23598588E+05 0.83572824E+01 0.26797709E+01 0.17698182E-01-0.13696261E-04    3
 0.71309904E-08-0.18750193E-11 0.23846239E+05 0.13654492E+02                   4

AlFCl2                  F   1Al  1Cl  2    0G   300.000  3000.000 1000.00    0 1
 0.89262287E+01 0.15524876E-02-0.91972793E-06 0.25106400E-09-0.26054340E-13    2
-0.98521501E+05-0.14053594E+02 0.46178514E+01 0.20320970E-01-0.32810708E-04    3
 0.24961084E-07-0.73052004E-11-0.97688714E+05 0.64677418E+01                   4

AlF2Cl                  F   2Al  1Cl  1    0G   300.000  3000.000 1000.00    0 1
 0.85115282E+01 0.21763672E-02-0.13044819E-05 0.36005015E-09-0.37744416E-13    2
-0.12290861E+06-0.13402724E+02 0.38839107E+01 0.21652207E-01-0.33358457E-04    3
 0.24550952E-07-0.70228933E-11-0.12198495E+06 0.87975267E+01                   4

ClAlF                   F   1Al  1Cl  1    0G   300.000  3000.000 1000.00    0 1
 0.62560909E+01 0.10839329E-02-0.64689117E-06 0.17778268E-09-0.18562111E-13    2
-0.52568646E+05-0.20390869E+01 0.35686777E+01 0.12609478E-01-0.19943411E-04    3
 0.14943838E-07-0.43262304E-11-0.52041813E+05 0.10802518E+02                   4

Al(OH)Cl2               H   1O   1Al  1Cl  2G   300.000  3000.000 1000.00    0 1
 0.11101832E+02 0.38975596E-03 0.28080833E-06-0.16032953E-09 0.22361318E-13    2
-0.90513162E+05-0.24411276E+02 0.37619375E+01 0.34843285E-01-0.61019978E-04    3
 0.48440238E-07-0.14391053E-10-0.89233895E+05 0.98909513E+01                   4

AlCl(OH)2               H   2O   2Al  1Cl  1G   300.000  3000.000 1000.00    0 1
 0.12876039E+02-0.12843833E-03 0.10679187E-05-0.45156395E-09 0.57656193E-13    2
-0.10657716E+06-0.34945130E+02 0.20324909E+01 0.51127126E-01-0.90080563E-04    3
 0.71452898E-07-0.21110341E-10-0.10472108E+06 0.15601968E+02                   4

ClAlOH 2A' trans        H   1O   1Al  1Cl  1G   300.000  3000.000 1000.00    0 1
 0.82931046E+01 0.33528713E-04 0.52337010E-06-0.23269608E-09 0.30349940E-13    2
-0.43961397E+05-0.12163385E+02 0.31102225E+01 0.25388843E-01-0.45915563E-04    3
 0.37310757E-07-0.11246602E-10-0.43107001E+05 0.11807602E+02                   4
```

```
AlCl2(CH3)              H   3C   1Al  1Cl  2G   300.000  3000.000 1000.00    0 1
 0.79959189E+01 0.11836732E-01-0.58893733E-05 0.14179411E-08-0.13415412E-12    2
-0.54670727E+05-0.49497326E+01 0.41325946E+01 0.29268026E-01-0.36438190E-04    3
 0.25674991E-07-0.74103561E-11-0.53949133E+05 0.13313648E+02                   4

AlCl(CH3)2              H   6C   2Al  1Cl  1G   300.000  3000.000 1000.00    0 1
 0.67056443E+01 0.22725936E-01-0.11248437E-04 0.26970825E-08-0.25437851E-12    2
-0.33021213E+05 0.15490120E+01 0.30899976E+01 0.39168878E-01-0.40347095E-04    3
 0.26028160E-07-0.73140929E-11-0.32348311E+05 0.18619304E+02                   4

AlCl(CH3) trans         H   3C   1Al  1Cl  1G   300.000  3000.000 1000.00    0 1
 0.54510255E+01 0.11201286E-01-0.55194094E-05 0.13178760E-08-0.12382189E-12    2
-0.73352980E+04 0.40951419E+01 0.31640747E+01 0.21819724E-01-0.24576238E-04    3
 0.16724021E-07-0.48046262E-11-0.69206656E+04 0.14837634E+02                   4

AlF2(OH)                H   1O   1F   2Al  1G   300.000  3000.000 1000.00    0 1
 0.99407738E+01 0.19817299E-02-0.64026033E-06 0.88872252E-10-0.34709244E-14    2
-0.13908290E+06-0.21118661E+02 0.29380683E+01 0.34075412E-01-0.56877057E-04    3
 0.44292240E-07-0.13061019E-10-0.13782077E+06 0.11808961E+02                   4

AlF(OH)2                H   2O   2F   1Al  1G   300.000  3000.000 1000.00    0 1
 0.11781703E+02 0.11709285E-02 0.40195107E-06-0.28886310E-09 0.42184533E-13    2
-0.13047757E+06-0.30019926E+02 0.28883542E+01 0.44357703E-01-0.78315915E-04    3
 0.63159939E-07-0.18982178E-10-0.12899565E+06 0.11191796E+02                   4

FAlOH trans             H   1O   1F   1Al  1G   300.000  3000.000 1000.00    0 1
 0.79345609E+01 0.58673254E-03 0.17648460E-06-0.13330165E-09 0.19600191E-13    2
-0.68172164E+05-0.11905604E+02 0.22834929E+01 0.27305536E-01-0.47509085E-04    3
 0.37685698E-07-0.11181566E-10-0.67199825E+05 0.14448530E+02                   4

Al(OH)2CH3              H   5C   1O   2Al  1G   300.000  3000.000 1000.00    0 1
 0.11510041E+02 0.11043443E-01-0.45304542E-05 0.90758819E-09-0.72064926E-13    2
-0.85671590E+05-0.25943886E+02 0.94307635E+00 0.59904551E-01-0.90019409E-04    3
 0.67570036E-07-0.19539700E-10-0.83810945E+05 0.23579586E+02                   4

Al(OH)(CH3)2            H   7C   2O   1Al  1G   300.000  3000.000 1000.00    0 1
 0.77848007E+01 0.23077537E-01-0.10923370E-04 0.25217553E-08-0.23033693E-12    2
-0.47642496E+05-0.41475331E+01 0.25035151E+01 0.48491102E-01-0.57325386E-04    3
 0.40210237E-07-0.11649081E-10-0.46739026E+05 0.20413597E+02                   4

CH3AlOH                 H   4C   1O   1Al  1G   300.000  3000.000 1000.00    0 1
 0.72604034E+01 0.10645100E-01-0.47012993E-05 0.10146979E-08-0.86914594E-13    2
-0.21673058E+05-0.48976921E+01 0.17160942E+01 0.37612495E-01-0.53860994E-04    3
 0.40609138E-07-0.11944746E-10-0.20752925E+05 0.20779802E+02                   4

HAl(OH)Cl               H   2O   1Al  1Cl  1G   300.000  3000.000 1000.00    0 1
 0.88443737E+01 0.44691215E-02-0.24271392E-05 0.63278685E-09-0.64069683E-13    2
-0.62125180E+05-0.17267019E+02 0.23962186E+01 0.31284011E-01-0.46476984E-04    3
 0.34080428E-07-0.98286007E-11-0.60810192E+05 0.13777210E+02                   4

HAl(CH3)Cl              H   4C   1Al  1Cl  1G   300.000  3000.000 1000.00    0 1
 0.60914428E+01 0.14379672E-01-0.73260448E-05 0.17988693E-08-0.17298125E-12    2
-0.24662685E+05 0.37355737E+00 0.25859658E+01 0.29597696E-01-0.33617630E-04    3
 0.22749876E-07-0.65449492E-11-0.23965716E+05 0.17125626E+02                   4
```

```
HAl(OH)CH3              H   5C   1O   1Al  1G   300.000  3000.000 1000.00    0 1
 0.75567870E+01 0.15380269E-01-0.78164726E-05 0.19246222E-08-0.18602149E-12    2
-0.40007574E+05-0.98202745E+01 0.12694315E+01 0.40984307E-01-0.49053346E-04    3
 0.32735676E-07-0.90768846E-11-0.38701204E+05 0.20578001E+02                   4

Al(OH)CH3Cl             H   4C   1O   1Al  1G   300.000  3000.000 1000.00Cl  1 1
 0.98597746E+01 0.11351939E-01-0.51867901E-05 0.11626264E-08-0.10360901E-12    2
-0.70741000E+05-0.17327961E+02 0.22921161E+01 0.45515312E-01-0.63999014E-04    3
 0.46567589E-07-0.13292062E-10-0.69364503E+05 0.18352437E+02                   4

AlO 2sigma              O   1Al  1    0    0G   300.000  3000.000 1000.00    0 1
 0.40662791E+01 0.63893725E-03-0.38505490E-06 0.10673806E-09-0.11228753E-13    2
 0.87438698E+04 0.29044572E+01 0.26721244E+01 0.64790440E-02-0.99318572E-05    3
 0.72566413E-08-0.20602817E-11 0.90225734E+04 0.95971936E+01                   4

HAlO 1sigma             H   1O   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.45685048E+01 0.39645995E-02-0.22629498E-05 0.60485141E-09-0.62035510E-13    2
-0.21550435E+04-0.73397689E+00 0.29472935E+01 0.98448109E-02-0.11003115E-04    3
 0.69293921E-08-0.19054115E-11-0.17730095E+04 0.73074891E+01                   4

H2AlO 2B2               H   2O   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.52456704E+01 0.63937942E-02-0.36311701E-05 0.96627379E-09-0.98725268E-13    2
 0.40225551E+04-0.21875809E+01 0.21553868E+01 0.18494659E-01-0.23033540E-04    3
 0.15829554E-07-0.45702163E-11 0.47083412E+04 0.12923108E+02                   4

AlC 4sigma-             C   1Al  1    0    0G   300.000  3000.000 1000.00    0 1
 0.42135758E+01 0.41316068E-03-0.24373056E-06 0.66227503E-10-0.68416101E-14    2
 0.85701877E+05 0.29441290E+01 0.28623424E+01 0.63756295E-02-0.10479462E-04    3
 0.80552179E-08-0.23713357E-11 0.85959438E+05 0.93616420E+01                   4

AlCH singlet            H   1C   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.48168916E+01 0.19396844E-02-0.73132567E-06 0.12662612E-09-0.79274019E-14    2
 0.78297243E+05-0.76572484E+01 0.29485705E+01 0.11952876E-01-0.20228611E-04    3
 0.16554905E-07-0.50837923E-11 0.78566166E+05 0.77698065E+00                   4

HAlCH 2A"               H   2C   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.58748077E+01 0.37969863E-02-0.17453199E-05 0.38717610E-09-0.33744342E-13    2
 0.61151832E+05-0.36825933E+01 0.34607270E+01 0.16619048E-01-0.27167299E-04    3
 0.22421270E-07-0.70538411E-11 0.61524370E+05 0.72925391E+01                   4

HAlCH2 singlet          H   3C   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.53234231E+01 0.84935526E-02-0.41564760E-05 0.98616020E-09-0.92117379E-13    2
 0.38511733E+05-0.17499040E+01 0.30905463E+01 0.19159666E-01-0.23760341E-04    3
 0.17127057E-07-0.50623861E-11 0.38905004E+05 0.86723492E+01                   4

H2AlCH 3A"              H   3C   1Al  1    0G   300.000  3000.000 1000.00    0 1
 0.65830172E+01 0.76056399E-02-0.39414956E-05 0.97999518E-09-0.95092792E-13    2
 0.53263093E+05-0.67423369E+01 0.33418400E+01 0.22106474E-01-0.29717300E-04    3
 0.21993811E-07-0.65927605E-11 0.53891868E+05 0.86538021E+01                   4

AlH2OCH3                H   5C   1O   1Al  1G   300.000  3000.000 1000.00    0 1
 0.51035642E+01 0.19634583E-01-0.10568041E-04 0.27173620E-08-0.27151701E-12    2
-0.26909281E+05 0.20288455E+01 0.29057191E+01 0.22896474E-01-0.77082618E-05    3
-0.39964891E-08 0.25185090E-11-0.26175184E+05 0.14059685E+02                   4
```

[a] Thermodynamic data are presented in the form of polynomial coefficients for the heat capacity (C_p), enthalpy (H) and entropy (S) as a function of temperature. These fits can be used with the CHEMKIN software package (Ref. 17) and are defined by:

$$C_p/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{H^\circ}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{S^\circ}{R} = a_1 \ln T + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

Note that $H^o = H^o(T) - H^o(298) + \Delta H_f^o(298)$, where $\Delta H_f^o(298)$ is the species heat of formation at 298 K, $H^o(T)$ is the standard enthalpy at temperature T, and $H^o(298)$ is the standard enthalpy at 298 K. Fits were carried out over two separate temperature ranges. The low, high, and break temperatures for these two fits are given at the end of the first line of the thermo data. For example, for the species AlH_3, the data were fit over the ranges 300 - 1000 K and 1000 - 3000 K. The subsequent three lines of numbers in the data record are the fitting parameters a_1 - a_7 for each fit. The parameters for the high-temperature range are given first, followed by those for the low-temperature range. More information concerning this format can be found in the CHEMKIN documentation (Ref. 17).

External Distribution

Dr. Carl Melius
LLNL
Building 132N, Room 2609

Dr. Charles Bauschlicher
NASA Ames Research Center
MS 230-3
Mountain View, CA 94305

Dr. Theodore M. Besmann
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6063

Dr. Donald R.F. Burgess, Jr.
Chemical Science and Technology Laboratory
NIST
Bldg. 221, Rm B312
Gaithersburg, MD 20899

Dr. Christopher E. Dateo
Thermosciences Institute
NASA Ames Research Center
MS 230-3
Moffett Field, CA 94035-1000

Dr. Suleyman A. Gokoglu
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44315

Dr. John W. Hastie
National Inst. Of Standards and Technology
Ceramics Division
B106/223
Gaithersburg, MD 20899

Dr. Wing Tsang
National Inst. Of Standards and Technology
Gaithersburg, MD 20899

Dr. Michael Zachariah
Dept. of Mechanical Engineering
Room 125
Minneapolis, MN 55455

Prof. Carmela Amato-Wierda
Dept. of Chemistry
University of New Hampshire
Durham, NH 03824

Prof. Timothy J. Anderson
Dept. of Chemical Engineering
University of Florida
P.O. Box 116005
Gainesville, FL 32611-6005

Prof. Peter B. Armentrout
Dept. of Chemistry
University of Utah
Henry Eyring Building
Salt Lake City, UT 84112

Prof. Richard Axelbaum
Dept. of Mechanical Engineering
Washington University
St. Louis, MO 63130

Prof. Eray S. Aydil
Chemical Engineering Dept.
University of California
Engineering Building II, Room 3334
Santa Barbara, CA 93106

Prof. C. Bernard
Laboratoire de Thermodynamique et Physico-Chimie
ENSEEG, BP75
38402 St. Martin D'Héres

Dr. Elisabeth Blanquet
LTPCM-ENSEEG
1130 rue de la oiscine
38402 Saint Martine D' Heres Cedex
France

Dr. Ken Brezinsky
Dept. of Chemical Engineering
University of Illinois at Chicago
Mail Code 110
Chicago, IL 60607

Dr. Stephanie Watts Butler
Manager, Advanced Process Control
Texas Instruments Inc.
P.O. Box 655012, MS 944
Dallas, TX 75243

Prof. Timothy Cale
Rensselaer Polytechnical Institute
Dept. of Chemical Engineering
6015 Center for Industrial Innovations
Troy, NY 12180-8676

Professor John W. Daily
Dept. of Mechanical Engineering
University of Colorado
Boulder, CO 80309

Biljana Cosic
Rensselaer Polytechnical Institute
Dept. of Chemical Engineering
6015 Center for Industrial Innovations
Troy, NY 12180-8676

Prof. David S. Dandy
Dept. of Agricultural and Chemical Engineering
Colorado State University
Fort Collins, CO 80523

Prof. Seshu B. Desu
Dept. of Materials Science and Engineering
Virgina Polytechnic Institute
213 Holden Hall
Blacksburg, VA 24061-0140

Prof. Demetre J. Economou
Dept. of Chemical Engineering
University of Houston
Houston, TX 77204-4792

Prof. Alexandre Ern
CERMICS, ENPC
6 et 8, avenue Blaise Pascal
77455 Marne la Vallee cedex 2
France

Prof. Dr. Roland A. Fischer
Lehrstuhl für Anorganische Chemie II
Ruhr-Universität Bochum
D-44780 Bochum Germany

Prof. Ellen R. Fisher
Dept. of Chemistry
Colorado State University
Fort Collins, CO 80523-1872

Prof. Arthur Fontijn
Dept. of Chemical Engineering
Rensselaer Polytechnical Institute
110 8th Street
Troy, NY 12180-3590

Prof. Steven George
Dept. of Chemistry
University of Colordao
Boulder, CO 80309

Prof. David G. Goodwin
Dept. of Mechanical Engineering and Applied Physics
California Institute of Technology
Mail Code 104-44
Pasadena, CA 91125

Prof. Mark S. Gordon
Dept. of Chemistry
Iowa State University
Spedding Hall 201
Ames, IA 50011

Professor Robert F. Hicks
Dept. of Chemical Engineering
University of California
5531 Boelter Hall
Los Angeles, CA 90095-1592

Prof. Roy G. Gordon
Dept. of Chemistry
Harvard University
12 Oxford Street
Cambridge, MA 02138

Dr. Frances A. Houle
Science & Technology for Storage Research
IBM
Almaden Research Center
San Jose, CA 95120-6699

Prof. Michael L. Hitchman
Dept. of Pure and Applied Chemistry
University of Strathclyde
295 Cathedral Street
Glasgow G1 1XL U.K

Prof. Klavs F. Jensen
Dept. of Chemical Engineering
Massachusetts Institute of Technology
Room 66-566
Cambridge, MA 02139

Prof. Stanislawa Jonas
Dept. of Ceramics
University of Mining and Metallurgy
Mickiewicza Street 30
30-059 Cracow Poland

Dr. Lev Kadinski
Lehrstuhl fur Strömungsmechanik
Friedrich-Alexander-Universität
Cauerstrausse 4
D-91058 Erlangen Germany

Prof. Robert J. Kee
Division of Engineering
Colorado School of Mines
Golden, CO 80401-1887

Prof. Keith King
Dept. of Chemical Engineering
University of Adelaide
Adelaide, SA Austrlia 5005

Prof. H. Komiyama
Dept. of Chemical Engineering
University of Tokyo
Hongo 7, Bunkyo-ku
Toyko 113 Japan

Dr. Anatoli A. Korkin
Advanced Systems Research Lab
Motorola inc.
MD M360
Mesa, AZ 85202

Dr. F. Langlais
Laboratoire des Composites
Thermostructuraux
Domaine Univesitaire
33600 Pessac
France

Dr. Woo Y. Lee
Stevens Institute of Technology
Department of Materials Science
Hoboken, NJ 07030

Prof. M.C. Lin
Dept. of Chemistry
Emory University
Atlanta, GA 30322

Prof. Paul Marshall
Dept. of Chemistry
University of North Texas
P.O. Box 5068
Denton, TX 76203-5068

Dr. Ellen Meeks
Product Development
Reaction Design
6440 Lusk Boulevard, D-209
San Diego, CA 92121

Prof. R.E. Mitchell
Dept. of Mechanical Engineering
Stanford University
Stanford, CA 94305

Prof. Philip W. Morrison, Jr.
Dept. of Chemical Engineering
Case Western Reserve University
10900 Euclid Avenue
Cleveland, OH 44106-7217

Prof. Triantafillos J. Mountziaris
Chemical Engineering Dept.
SUNY Buffalo
Buffalo, NY 14260

Dr. Roger Naslain
Laboratoire des Compsites Thermostructuraux
Domaine Universitaire
33600 Pessac France

Dr. Michel Pons
Laboratoire de Thermodynamique et Physico-Chimie
Institut National Polytechnique de Grenoble
ENSEEG
38402 Saint-Martin-D-Heres Cedex
France

Prof. Martyn E. Pemble
Dept. of Chemistry
University of Salford
Salford M5 4WT U.K.

Dr. Daniel E. Rosner
Chemical Engineering Dept.
Yale University
P.O. Box 2159, Yale Station
New Haven, CT 06520-2159

Dr. Amy Rovelstad
Corning Inc.
SP-TD-01-2
Corning, NY 14831

Prof. Robert J. Santora
Dept. of Mechanical Engineering
Pennsylvania State University
313A Mechanical Engineering Building
University Park, PA 16802

Prof. Adel Sarofim
REI
77 W. 200 South, Suite 120
Salt Lake City, UT 84101-3201

Prof. Selim Senkan
Chemical Engineering Dept.
UCLA
5531 Boelter Hall, KE2R
Los Angeles, CA 90024-1592

Dr. Y. Shimogaki
Dept. of Materials Engineering
University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656
Japan

Mr. John A. Sopko
PPG Industries
Glass Technology Center
Pittsburgh, PA 15238-0472

Prof. Stratis V. Sotirchos
Dept. of Chemical Engineering
University of Rochester
Rochester, NY 14627-0166

Prof. Karl E. Spear
Dept. of Ceramic Science and Engineering
Pennsylvania State University
201 Steidle Building
University Park, PA 16802

Prof. Thomas L. Starr
Room 113
Baker Building
Georgia Institute of Technology
Atlanta, GA 30332-0245

Prof. Gerald B. Stringfellow
College of Engineering
University of Utah
1495 East 100 South
Salt Lake City, UT 84112-1109

Prof. Mark T. Swihart
Dept. of Chemical Engineering
University of Buffalo
907 Furnas Hall
Buffalo, NY 14260

Prof. Francis Teyssandier
CNRS/IMP, UP 8521
Université, Avenue de Villeneuve
66860 Perpignan Cédex
France

Prof. Richard K. Ulrich
University of Arkansas
Fayetteville, AR 72701

Prof. Constantin Vahlas
Centre Interuniversitaire de Recherche et Dingenierie des
Ecole Nationale Superieure de Chimie de Toulouse
118 Route de Narbonne
31077 Toulouse cedex 4 France

Prof. Stan Veprek
Institute for Inorganic Materials
Technical University of Munich
Lichtenbergstrasse 4
D-85747 Garching
Germany

Prof. Jürgen Warnatz
Interdiziplinares Zentrum für Wissenschaftliches Rechen
Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 368
D-69120 Heidelberg
Germany

Prof. Dr. Jürgen Wolfrum
Physikalisch-Chemisches Institut
Ruprecht-Karls-Universität Heidelberg
IM Neuenheimer Feld 253
69120 Heidelberg, Germany

Prof. Margaret Wooldridge
University of Michigan
Dept. of Mechanical Engneering and Applied
Ann Harbor, MI 48109-2125

Prof. H. Bernard Schlegel
Dept. of Chemistry
Wayne State University
Room 365
Detroit, MI 48202

Dr. Thomas H. Baum
Advanced Technology Materials
7 Commerce Drive
Danbury, CT 06810-4169

Dr. H.F. Calcote
Director of Research
Chemlon, Inc.
P.O. Box 12
Princeton, NJ 08542

Dr. Jitendra S. Goela
Rohm and Haas Advancd Materials
185 New Boston Street
Woburn, MA 01801-6278

Dr. Ilan Golecki
Allied Signal, Inc.
101 Columbia Road
Morristown, NJ 07962

Dr. Donald L. Hildenbrand
SRI International
AG231
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. Francis Maury
Laboratoire des Materiaux
Institut National Polytechique
118 route de Narbonne
31077 Toulsouse Cedex 4
France

Dr. Richard J. McCurdy
Pilkington LOF
20th and Center Street
Ottawa, IL 61350

Dr. Meyya Meyyappan
NASA Amed Research Center
Mailstop 229-3
Moffat Field, Ca 94035

Dr. Duane A. Outka
Lam Research Corporation
Mailstop CA3
Fremont, CA 94538

Dr. Michelle T. Schulberg
Novellus Systems Inc.
3970 North First Street
San Jose, CA 95134

Prof. Irene R. Slagle
Dept. of Chemistry
Catholic University
201 Maloney Hall
Washington, D.C. 20064

Prof. Robin Walsh
Dept. of Chemistry
University of Reading
Whiteknights
Reading RG6 2AD U.K.

Dr. Bruce H. Weiller
Mechanics and Materials Technology Center
Aerospace Corporation
P.O. Box 92957
Los Angeles, CA 90009-2957

Dr. Svetlana M. Zemskova
Institute of Inorganic Chemistry
Siberian Branch, Russian Academy of Sciences
3, Ac. Lavrentyev Ave.
Novosibirsk 6300
Russia

Sandia Internal Distribution:

MS 9052	M.D. Allendorf, 8361 (10 copies)
MS 0601	W.G. Breiland, 1126
MS 0601	M.E. Coltrin, 1126
MS 9018	Central Technical Files, 8945-1 (3copies)
MS 0899	Technical Library, 9616
MS 9021	Classification Office, 8511