

Temperature effect on the thermochemical properties of the AlX_3 Lewis acids: DFT study ($X= H, F, Cl$ and Br)

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ABSTRACT

The thermochemical properties of AlX_3 Lewis acids have been characterized in detail under the temperature effect change using the DFT method as well as the *ab initio* method. Thermochemical properties subject of study are internal thermal energy U° , enthalpy H° , entropy S° , Gibbs free energy G° in addition to the volumetric heat capacity C_v° at ambient pressure. All these properties were examined at different fixed temperatures T ranging 300 K and 1200 K. Considering the electronic energy, stability of AlX_3 halide increases according to the trend $AlBr_3 > AlCl_3 > AlF_3 > AlH_3$. This is further confirmed by the Gibbs free energy G° values as a T -function. Gibbs free energy G° is a decreasing function when T increases against the other energy quantities which increase with T . ZPE taken into account or not, the electronic energy is not affected by the change in temperature. The reaction internal energy $\Delta_r U^\circ$, the reaction enthalpy $\Delta_r H^\circ$, the reaction entropy $\Delta_r S^\circ$ and the reaction Gibbs free energy $\Delta_r G^\circ$ for all the AlX_3 -forming reaction were deduced from the results of calculations at each temperature of the study interval. This allowed to define a new type of redox couples X_2 / AlX_3 where aluminum halide, which here is a reducing species, acts as a donor of the particle exchanged Al aluminum atom. It was established that AlF_3 is the strongest reducing while the strongest oxidant is molecular hydrogen H_2 . It was also showed that, at each temperature, the AlX_3 formation reaction from Al and X_2 was highly exothermic.

Keywords: Ab-initio, Aluminum, DFT, Temperature, Thermochemical properties.

INTRODUCTION

In recent years, several new hydrides of group 13 elements such as aluminum-containing compounds have received special attention because they play an important role in the manufacturing process of new materials and synthetic chemistry [1-9]. Among these important compounds, a considerable importance has been given to the chemistry of the donor-acceptor alane complexes because of their importance in chemical catalysis and elementary chemistry and also because of their structural richness and their potential to act as metal sources in chemical vapor deposition (CVD) processes [10-15]. Thus, the knowledge of their complexation energies and their stability would be very useful for a quantitative description of their reactivity, reaction mechanisms and also their applications. These compounds are also of major importance for living beings, and new optical materials [16-18]. In previous works, hydrides of aluminum AlX_3 have been the subject of various published papers of our group [19-22].

To the best of our knowledge, no comparative study about the temperature effect on the thermodynamic properties of these compounds has been published in spite of the abundance of structural and energetic data in literature. Taking into account the multiple possibilities to form types of donor-acceptor complexes by the 13th group elements, it can be considered that the chemistry of such elements deserve more interest by the experimental as well as by the theoretical approaches.

In this work, the study will focus on the temperature impact on the thermochemical properties of AlX_3 Lewis acids and secondly these results will be used for assessing the energy quantities relating to the reaction between Al and X_2 ($\text{X}=\text{H}, \text{F}, \text{Cl}$ and Br) whose chemical equation is:



and consequently classify these halides in order to increase chemical stability based on the determination of the reaction free enthalpy or Gibbs free energy of reaction. The heat exchange of the reaction is also evaluated.

DFT is the method used in this work. This method leads in most cases to results that are consistent with the experimentation [23-26].

MATERIALS AND METHODS

Computational Details

Geometrical optimization was performed using Gaussian 09 [27]. DFT calculations employed a combination of local gradient-correction and exact exchange functional according to the prescription of Becke [28, 29] and the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP) [30-33]. This has been undertaken using a 6-311G (d,p) basis set. The geometry optimizations of all entities studied in this work using the DFT method at the previously cited level of theory were followed by harmonic vibrational frequency calculations at different temperatures selected in the interval [300 K, 1200 K] with a step of 100 K. Harmonic vibrational calculations were performed in order to identify, at each temperature, the nature of the structures on the potential surface and computing the various thermochemical properties of aluminum halides AlX_3 ($\text{X}=\text{H}, \text{F}, \text{Cl}$ and Br). Whatever the temperature of the selected interval, entities possess all real frequencies. The zero-point energy (ZPE) corrections were carried out at the B3LYP/6-311G (d,p) level. The ZPEs were scaled up by the factor 0.9153 [34]. In order to improve accuracy of the energetic results, single point calculations were performed based on the B3LYP/6-311G (d,p) optimized geometries at the CCSD(T)/6-311G(d,p) level. Final energies were calculated at the CCSD(T)/6-311G (d,p)//B3LYP/6-311G(d,p)+ZPE level. The electronic structure has been done using the natural bond orbital (NBO) partitioning analysis [35].

RESULTS AND DISCUSSION

Geometries

AlX_3 ($\text{X}=\text{H}, \text{F}, \text{Cl}$ and Br) Lewis acids are electron acceptors having a flat geometry which is compatible with the symmetry D_{3h} . The depicted geometrical parameters are reported in figure 1.

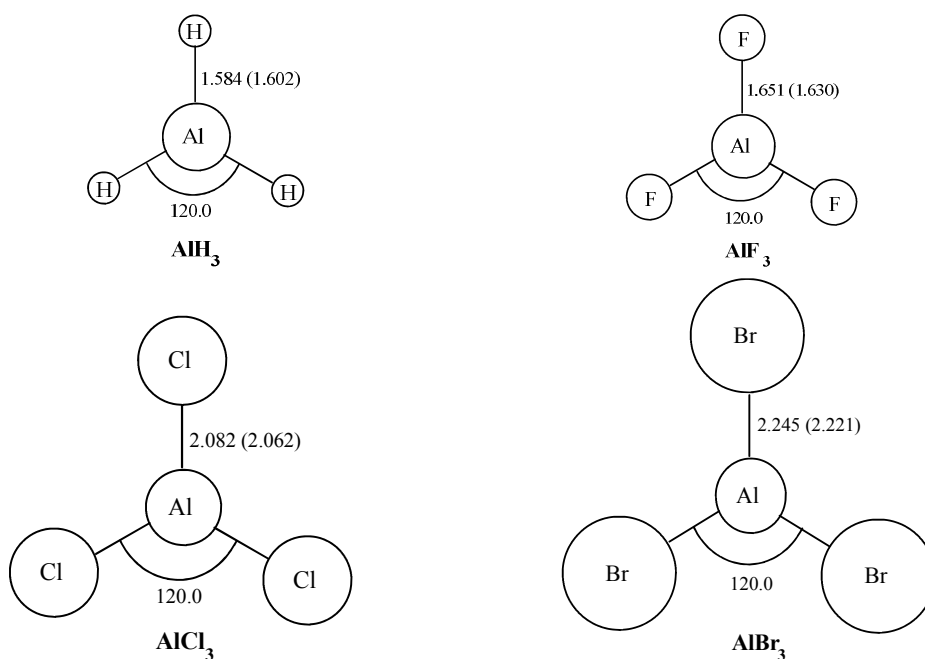


Figure 1: Optimized geometries of alane AlH_3 and aluminum halides AlX_3 ($\text{X}=\text{F}, \text{Cl}$ and Br). Experimental gas phase values are given in parentheses (from [36-37]). Bond lengths are in Å and bond angles in degrees.

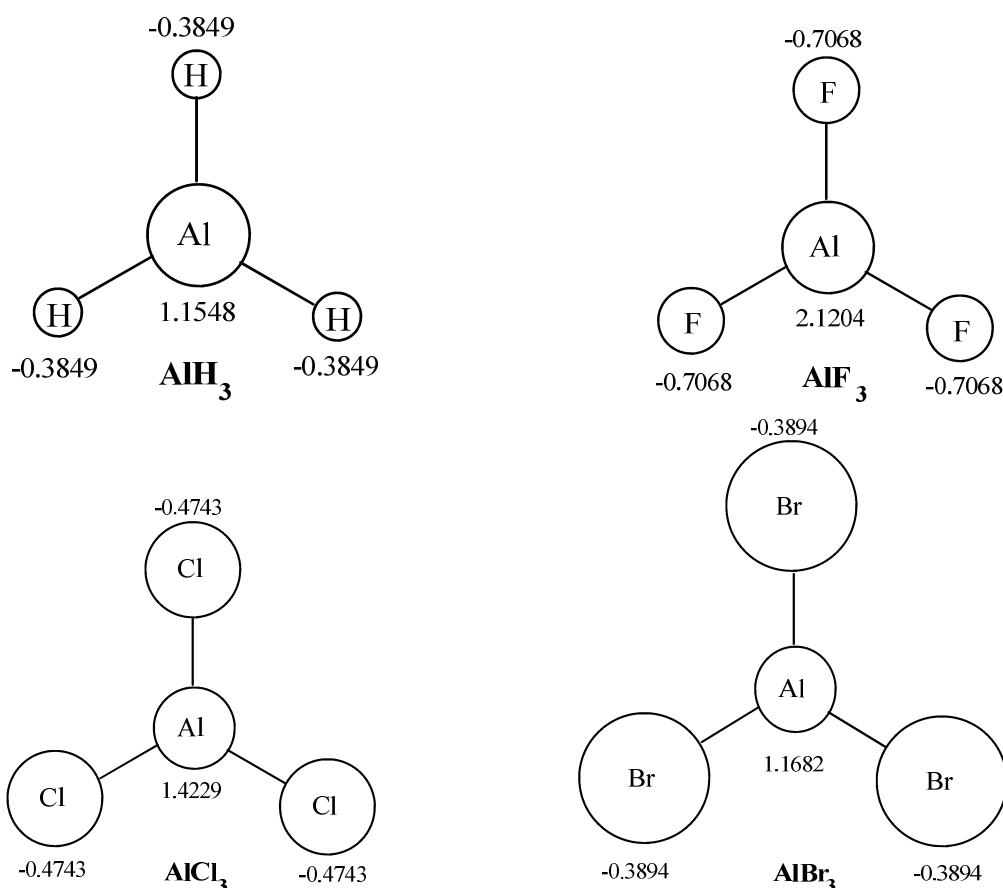


Figure 2: Net charges carried by the halogen atoms of each halide and aluminum determined by NBO calculation at B3LYP/6-311G(d,p) level.

In each halide, as shown in figure 2, the positive charge is carried by the central atom of aluminum, while the negative against load is evenly distributed on the peripheral hydrogen and halogen atoms which is consistent with the difference in electronegativity between Al and X (X = H, F, Cl and Br). Aluminum is less electronegative than the other chemical elements presented in this study as it is shown by table 1

Table 1: Pauling electronegativity for chemical elements presented in this study [38]

Chemical elements	H	Al	F	Cl	Br
Electronegativity	2.2	1.6	4.0	3.2	3.0

Thermochemical properties

The overall energy values E_0 , E_{ZPE} , U° , G° and H° ($\text{kJ}\cdot\text{mol}^{-1}$), entropy S° ($\text{J}\cdot\text{K}\cdot\text{mol}^{-1}$) and heat capacity C_v° ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) + ZPE level of all implied stationary points are summarized in Tables 2-5. These results are determined at different temperatures and under ambient pressure ($P^\circ=1.013\times 10^5$ Pa).

Table 2: Energy quantities ($\text{kJ}\cdot\text{mol}^{-1}$) E_0 at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, E_{ZPE} , U° , H° , G° , entropy ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) S° and volumetric heat capacity ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) C_v° , at the B3LYP/6-311G(d,p) level of theory of AlH_3 in the temperature range [300K, 1200K]

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E_0 ($\text{kJ}\cdot\text{mol}^{-1}$)	-243.74	-243.74	-243.74	-243.74	-243.74	-243.74	-243.74	-243.74	-243.74	-243.74
E_{ZPE} ($\text{kJ}\cdot\text{mol}^{-1}$)	48.73	48.73	48.73	48.73	48.73	48.73	48.73	48.73	48.73	48.73
U° ($\text{kJ}\cdot\text{mol}^{-1}$)	56.87	60.63	64.86	69.55	74.65	80.10	85.84	91.83	98.02	104.38
H° ($\text{kJ}\cdot\text{mol}^{-1}$)	59.35	63.96	69.01	74.54	80.47	86.75	93.33	100.15	107.17	114.36
G° ($\text{kJ}\cdot\text{mol}^{-1}$)	-4.17	-24.25	-46.88	-70.57	-95.22	-120.74	-147.07	-174.15	-201.91	-230.33
S° ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	213.04	220.52	231.79	241.84	250.98	259.36	267.11	274.29	280.98	287.24
C_v° ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)	3.96	39.71	44.68	49.06	52.85	56.06	58.74	60.97	62.81	64.34

Table 3: Energy quantities (kJmol^{-1}) E_0 at the CCSD(T)/6-311G(d,p)/B3LYP/6-311G(d,p) level of theory, E_{ZPE} , U° , H° , G° , entropy ($\text{JK}^{-1}\text{mol}^{-1}$) S° and volumetric heat capacity ($\text{JK}^{-1}\text{mol}^{-1}$) C_v° at the B3LYP/6-311G(d,p) level of theory of AlF_3 in the temperature range [300K, 1200K]

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E_0 (kJmol^{-1})	-541.25	-541.25	-541.25	-541.25	-541.25	-541.25	-541.25	-541.25	-541.25	-541.25
E_{ZPE} (kJmol^{-1})	20.24	20.24	20.24	20.24	20.24	20.24	20.24	20.24	20.24	20.24
U° (kJmol^{-1})	31.97	37.79	43.99	50.53	57.30	64.21	71.25	78.36	85.53	92.76
H° (kJmol^{-1})	34.44	41.11	48.15	55.52	63.12	70.87	78.73	86.67	94.68	102.74
G° (kJmol^{-1})	-48.51	-77.86	-108.41	-140.41	-173.67	-208.02	-243.35	-279.56	-316.58	-354.32
S° ($\text{JK}^{-1}\text{mol}^{-1}$)	278.24	300.79	313.13	326.55	338.26	348.60	357.86	366.23	373.87	380.87
C_v° ($\text{JK}^{-1}\text{mol}^{-1}$)	54.00	59.96	63.94	66.63	68.49	69.81	70.76	71.48	72.02	72.45

Table 4: Energy quantities (kJmol^{-1}) E_0 at the CCSD(T)/6-311G(d,p)/B3LYP/6-311G(d,p) level of theory, E_{ZPE} , U° , H° , G° , entropy ($\text{JK}^{-1}\text{mol}^{-1}$) S° and volumetric heat capacity ($\text{JK}^{-1}\text{mol}^{-1}$) C_v° at the B3LYP/6-311G(d,p) level of theory of AlCl_3 in the temperature range [300K, 1200K]

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E_0 (kJmol^{-1})	-1621.17	-1621.17	-1621.17	-1621.17	-1621.17	-1621.17	-1621.17	-1621.17	-1621.17	-1621.17
E_{ZPE} (kJmol^{-1})	12.51	12.51	12.51	12.51	12.51	12.51	12.51	12.51	12.51	12.51
U° (kJmol^{-1})	26.53	33.22	40.10	47.17	54.34	61.59	68.89	76.22	83.58	90.96
H° (kJmol^{-1})	29.01	36.55	44.26	52.16	60.16	68.24	76.37	84.53	92.72	100.93
G° (kJmol^{-1})	-64.55	-97.66	-132.10	-168.11	-205.45	-243.95	-283.46	-323.88	-365.11	-407.10
S° ($\text{JK}^{-1}\text{mol}^{-1}$)	313.80	335.51	352.75	367.10	379.44	390.23	399.80	408.40	416.21	423.35
C_v° ($\text{JK}^{-1}\text{mol}^{-1}$)	63.36	67.57	69.91	71.26	72.15	72.75	73.17	73.47	73.70	73.88

Table 5: Energy quantities (kJmol^{-1}) E_0 at the CCSD(T)/6-311G(d,p)/B3LYP/6-311G(d,p) level of theory, E_{ZPE} , U° , H° , G° , entropy ($\text{JK}^{-1}\text{mol}^{-1}$) S° and volumetric heat capacity ($\text{JK}^{-1}\text{mol}^{-1}$) C_v° at the B3LYP/6-311G(d,p) level of theory of AlBr_3 in the temperature range [300K, 1200K]

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E_0 (kJmol^{-1})	-7959.71	-7959.71	-7959.71	-7959.71	-7959.71	-7959.71	-7959.71	-7959.71	-7959.71	-7959.71
E_{ZPE} (kJmol^{-1})	9.49	9.49	9.49	9.49	9.49	9.49	9.49	9.49	9.49	9.49
U° (kJmol^{-1})	24.99	32.00	39.09	46.31	53.60	60.93	68.30	75.69	83.09	90.51
H° (kJmol^{-1})	27.47	35.32	43.25	51.30	59.42	67.58	75.78	84.00	92.24	100.49
G° (kJmol^{-1})	-76.36	-113.03	-151.04	-190.65	-231.62	-273.75	-316.91	-360.98	-405.88	-451.53
S° ($\text{JK}^{-1}\text{mol}^{-1}$)	348.26	370.89	388.57	403.24	415.76	426.66	436.32	444.98	452.83	460.01
C_v° ($\text{JK}^{-1}\text{mol}^{-1}$)	67.11	70.10	71.66	72.57	73.14	73.53	73.79	73.99	74.13	74.24

An initial examination of previously prepared tables shows that, whatever the halide, both electronic energy E_0 and zero-point energy E_{ZPE} are not influenced by the temperature, which is not the case for other quantities. To know how the temperature acts on the total energy E_{tot} , it can be calculated by the following formula $E_{\text{tot}} = E_0 + U^\circ$, thus obtaining table 6 with U° the internal thermal energy.

Table 6: Total energies (kJmol^{-1}) E_{tot} at the CCSD(T)/6-311G(d,p)/B3LYP/6-311G(d,p) + ZPE level of theory of the alane AlH_3 and the three aluminum halides AlX_3 ($X = \text{F}, \text{Cl}, \text{and Br}$) whatever T in [300K, 1200K] temperature range

	AlH_3	AlF_3	AlCl_3	AlBr_3
$E_{\text{tot}}(\text{kJmol}^{-1})$	-6.40×10^5	-1.42×10^6	-4.26×10^6	-2.09×10^7

The results of our calculations show, after being transformed into graphs, that total energy is not affected by the temperature variation regardless of the aluminum halide (figure 3). All representative points are aligned in finding very low slope whose average does not exceed the following value $0.059 \text{ kJ.K}^{-1}.\text{mol}^{-1}$.

The rigorous linearity of all points found is reflected in the values of the regression coefficient R^2 approaching 1 for all aluminum halides studied. It is also important to note that the figure 3 shows that AlBr_3 is the most stable halide electronically. Furthermore, AlBr_3 has a high electronic energy stability compared to other halides. It is due to the fact that isolated AlX_3 strong π -donation from the halogen lone pairs into the formally empty p (π) orbital at aluminum stabilizes the molecule from AlBr_3 to AlH_3 according to the trend $\text{AlBr}_3 > \text{AlCl}_3 > \text{AlF}_3 > \text{AlH}_3$.

The enthalpy function H° corresponds to the total energy of a thermodynamic system. It includes the internal energy which is the energy needed to form the system, to which is added the work that this system must exercise against the external pressure to fill its volume. As for the internal energy U° , it corresponds to the intrinsic energy of the system, defined on a microscopic scale, to the exclusion of kinetic or potential energy of the system interaction with its environment.

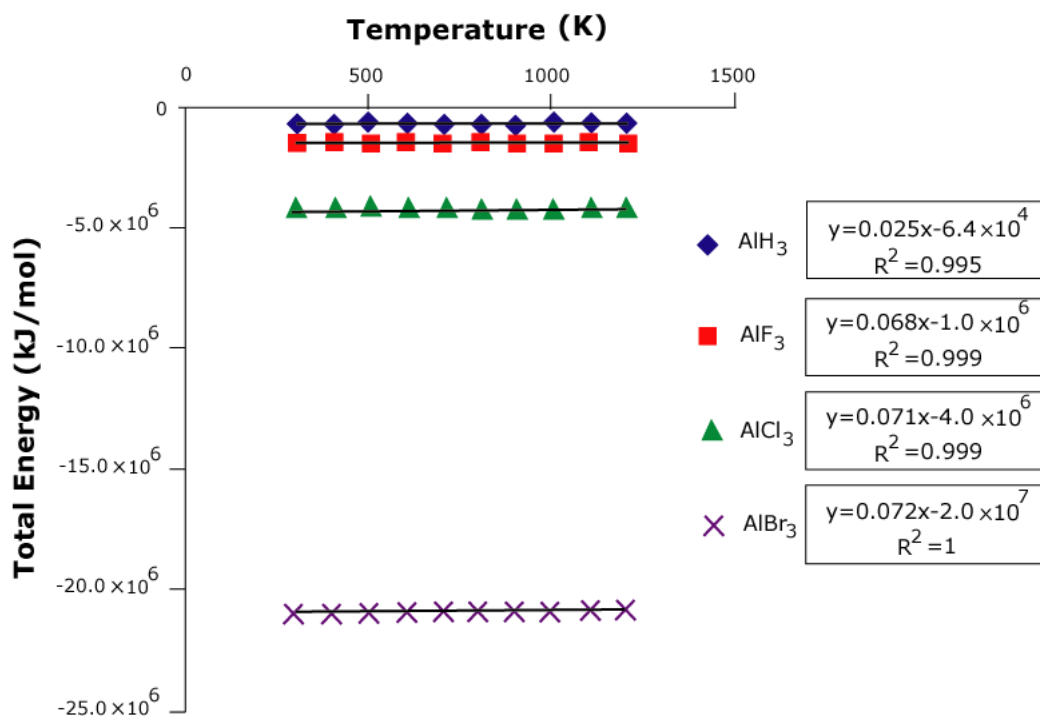


Figure 3: Graphical representation of the total energy for different temperatures at B3LYP/6-311G (d,p) level of calculation for the three aluminum halides and alane.

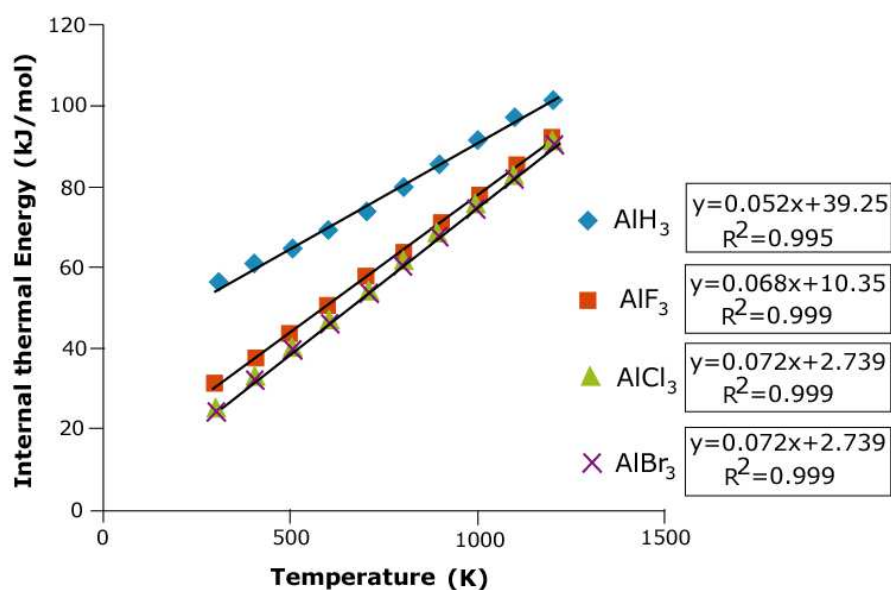


Figure 4: Graphical representation of the thermal energy for different temperatures at B3LYP/6-311G (d,p) level of calculation for the three aluminum halides.

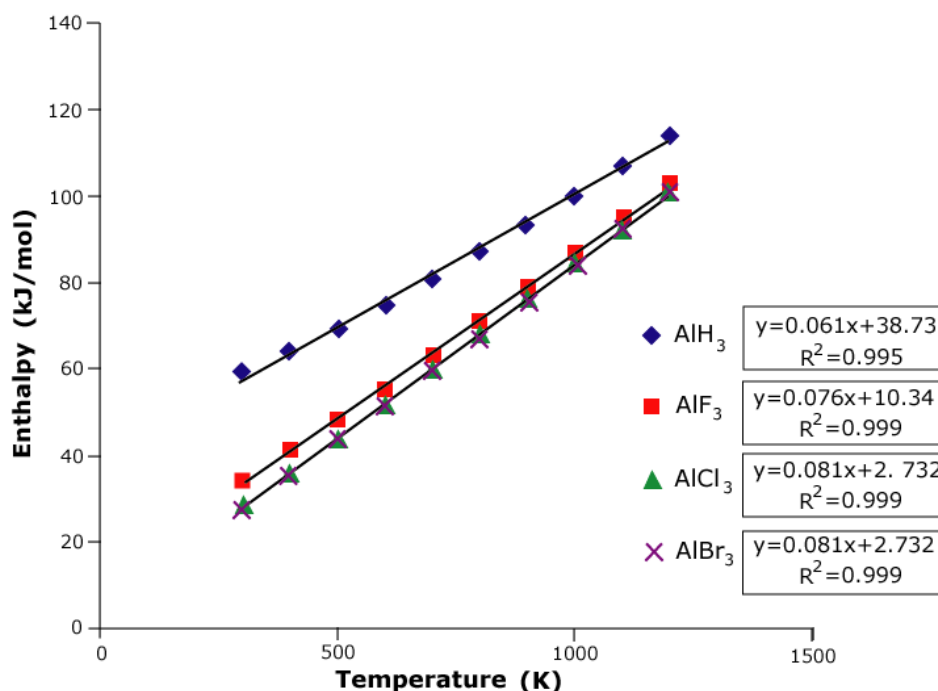


Figure 5: Graphical representation of the enthalpy at different temperatures at B3LYP/6-311G(d,p) level of calculation for the three aluminum halides and alane.

Examining the results for these two energy quantities shows that enthalpy H° and internal thermal energy U° evolve in the same direction when the temperature grows as it is shown in figures 4 and 5. It can be noted a slight shift between the three halides what is compatible with very close thermal behaviors by these three entities and AlH_3 is an exception.

Figure 6 shows, on one hand, that the entropy of different aluminum halide increases with temperature. On the other hand, AlBr_3 has the highest values of entropy at any temperature in the selected range. The following trend $S(\text{AlBr}_3) > S(\text{AlCl}_3) > S(\text{AlF}_3) > S(\text{AlH}_3)$ is noted. This trend is consistent with the volume of the studied entities, in other words, with their total number of electrons.

Table 6: Account the total number N of electrons in the species studied

Species	AlH_3	AlF_3	AlCl_3	AlBr_3
N (electrons)	16	40	64	118

Indeed, table 6 gives the total number of electrons in each halide. Since entropy is a measure of disorder, it is obvious that AlBr_3 has the highest entropy as it is the molecule that has the largest number of possible complexions or combinations to deliver these electrons. This is consistent with the statistical interpretation of entropy which characterizes the degree of disorganization or lack of information from one system.

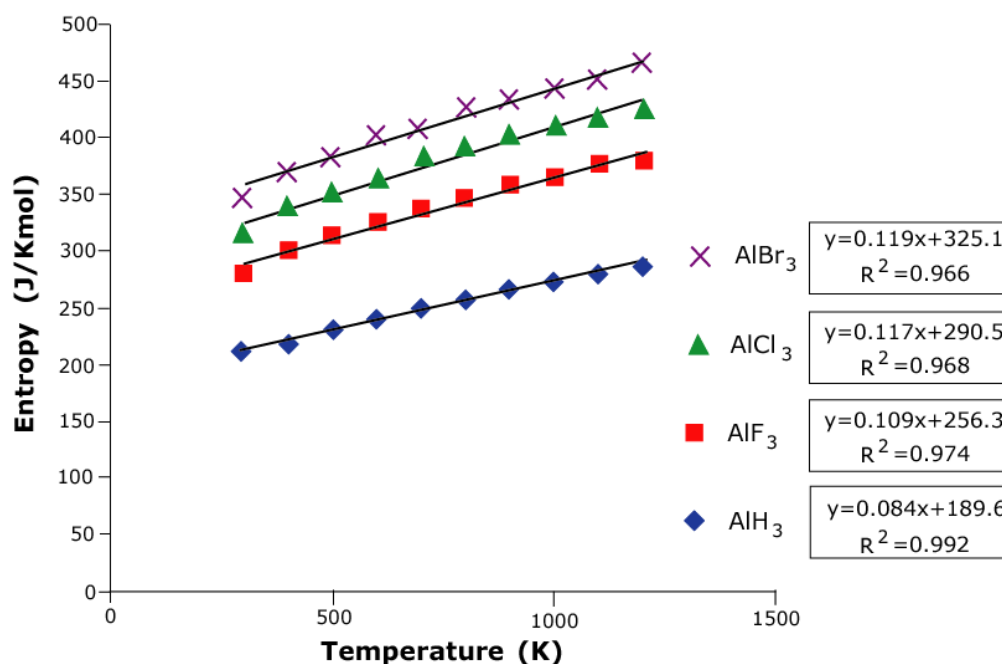


Figure 6: Graphical representation of the entropy at different temperatures at B3LYP/6-311G(d,p) level of calculation for the three aluminum halides and alane.

In this context entropy, it can be concluded that AlBr_3 is the most disorderly system, followed by AlCl_3 and AlF_3 and finally comes AlH_3 alane. According to the second principle of thermodynamics, a spontaneous or natural evolution occurs with creation of entropy, therefore if there is a possibility of spontaneous formation of an aluminum halide AlX_3 ; AlBr_3 will have the greatest chance of being. Then it is another way to confirm its relative stability compared to the other species studied.

Now comes the turn of the Gibbs free energy. The Gibbs free energy G° behaves in fact as a potential function and integrates the behavior of the external environment. The results for G° in this study show that it takes negative values over the chosen interval (figure 7).

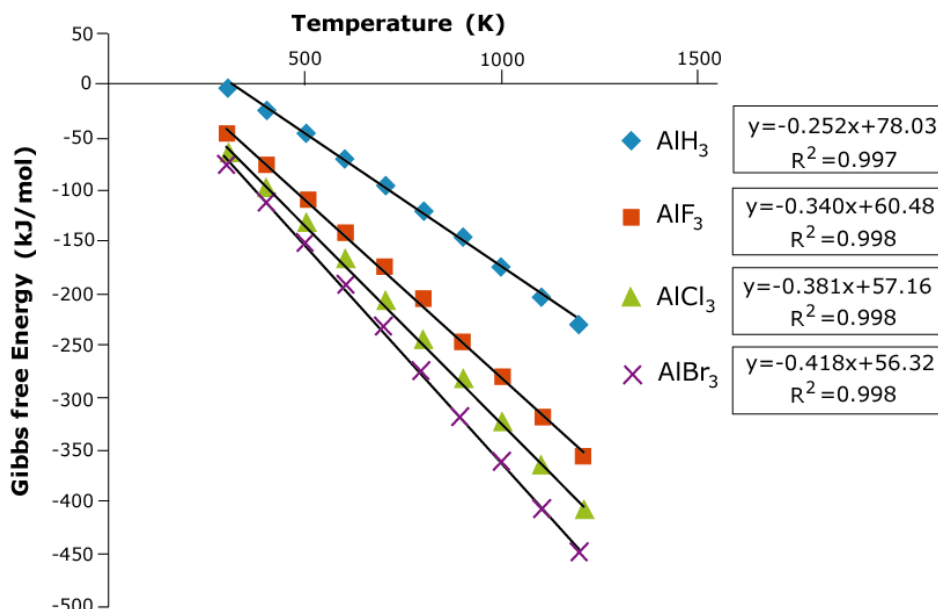


Figure 7: Graphical representation of the Gibbs free energy at different temperatures at B3LYP/6-311G(d,p) level of calculation for the three aluminum halides and alane.

The Gibbs free energy $G^\circ(T)$ of these halides is a straight line, with negative slope, since all points are aligned and this is confirmed by the correlation coefficients that almost reach their maximum value. It is important to note once again the chemical stability of AlBr_3 compared to other aluminum halides and alane AlH_3 . The chemical stability gap between AlBr_3 in one side and the two entities AlCl_3 and AlF_3 in the other side is very low at low temperatures and increases gradually as the temperature rises. AlH_3 remains the compound chemically less stable of all. In any case, the Gibbs free energy takes increasingly negative values with increasing temperature. This effect implies an increase of the relative stability of halides studied. G° is thus a thermodynamic potential which further confirms the stability of AlBr_3 compared to other aluminum halides and AlH_3 .

AlX_3 ($\text{X}=\text{H}, \text{F}, \text{Cl}$ and Br) are molecules. Molecules are more or less complex sets of atoms connected together by bonds; thermal agitation submits these constraints in three different ways: by rotation; by stretching and by changing the bond angle. These three movements are three internal degrees of freedom of each bond. For this reason, the molecules have a different behavior of monatomic substances (consisting of isolated atoms, such as argon or neon) which only have three degrees of freedom of translational movement. Although the agitation of atoms in the molecules is described as internal, it nevertheless produced an overall agitation of the molecule (like a balloon floating on water); thus, there is a potential transfer in both directions between bustle of external translation of the molecule and the internal agitation of molecular bonds.

When we subtract the heat to molecules, their temperature is reduced in proportion to the number of degrees of freedom, (in order wise their translational kinetic energy) and internal agitation energy. This phenomenon results from the principle of equipartition theorem, according to which, for any system in equilibrium, the kinetic energy is distributed evenly between all degrees of freedom. At any temperature, the total energy is greater than the only translational kinetic energy (translated by temperature); conversely, for every increase in temperature, a portion of the energy imparted to the molecules is stored as internal energy molecules (in the form of agitation of atomic bonds). This portion of kinetic energy absorbed by the intramolecular movement increases the internal energy of each molecule at a given temperature. This property is called heat capacity of the molecule.

The volumetric heat capacity is the amount of energy required to raise a unit volume of a substance by a unit temperature. The thermal evolution of the constant volume heat capacity of each species studied in this work is given in figure 8. The curves shown in figure 8 allow to note a clear divergence between the alane AlH_3 and AlX_3 ($\text{X}=\text{F}, \text{Cl}, \text{Br}$) halides thermal behavior. The C_v° values are more important for the halides AlX_3 as alane AlH_3 .

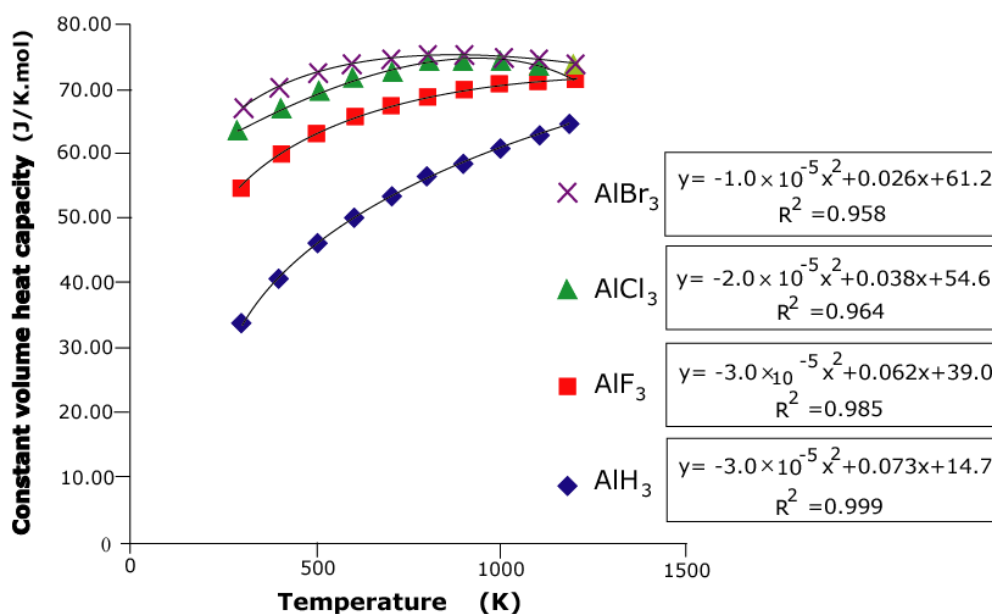


Figure 8: Graphical representation of the volumetric heat capacity at different temperatures at B3LYP/6-311G(d,p) level of calculation for the three aluminum halides and alane.

Here it is reported that the theoretical methods used to calculate C_v° take into account the contribution of different degrees of freedom. No method currently provides only really satisfactory results, directly usable in applied sciences. For most compounds and especially gaseous C_v° are increasing functions of the temperature. Apart from very simple cases where statistical mechanic is used to determine C_v , mostly must use empirical equation of the type

$$C_v^\circ = a + bT + cT^2 \quad (2)$$

The equations of the curves shown in figure 8 confirm that the use of empirical equations generalized by the equation (2) was plausible. The coefficient values are shown in table 7 and are characteristic of a given compound.

Table 7: Theoretical values determined for the coefficients of the empirical development of the volumetric heat capacity as a function of temperature at the B3LYP/6-311G (d,p) level of theory

	a (J.K ⁻¹ .mol ⁻¹)	b (J.K ⁻² .mol ⁻¹)	c (J.K ⁻³ .mol ⁻¹)
AlH₃	14.7	0.073	1.0 × 10 ⁻⁵
AlF₃	39.0	0.062	2.0 × 10 ⁻⁵
AlCl₃	54.6	0.038	3.0 × 10 ⁻⁵
AlBr₃	61.2	0.026	3.0 × 10 ⁻⁵

Energetic parameters of reaction

In this section we will use these results to generate various thermochemical informations. We have run calculations for each of the reactants and products in the reaction (1) where an aluminum Al atom fix three X atoms from the molecular entities X₂.

The usual way to calculate Δ_rU° the internal energies, Δ_rH° the enthalpies and Δ_rG° the Gibbs free energies of reaction is to calculate energies of formation, and take the appropriate sums and difference.

$$\Delta_r Y^\circ(T) = \sum_{\text{products}} \Delta_f Y^\circ_{\text{prod}}(T) - \sum_{\text{reactants}} \Delta_f Y^\circ_{\text{react}}(T) \quad (3)$$

with Y°=U°, H° or G°. However, it is possible to use the calculation results provided from the end of treatment with gaussian package according to the following

$$\Delta_r Y^\circ(T) = \sum_{\text{products}} [E_0 + Y^\circ(T)] - \sum_{\text{reactants}} [E_0 + Y^\circ(T)] \quad (4)$$

with E₀ is the total electronic energy and Y°=U°, H° or G°.

To calculate Δ_rS° the entropy of reaction, there is a choice between two methods. Let us use equation (4) with a slight modification as it is shown by equation (5)

$$\Delta_r S^\circ(T) = \sum_{\text{products}} \left[\frac{E_0}{T} + S^\circ(T) \right] - \sum_{\text{reactants}} \left[\frac{E_0}{T} + S^\circ(T) \right] \quad (5)$$

or one benefits from the preceding results concerning the values from Δ_rH° and Δ_rG° at each temperature is then

$$\Delta_r S^\circ(T) = \frac{\Delta_r H^\circ(T) - \Delta_r G^\circ(T)}{T} \quad (6)$$

For this, we need the data determined for the reactants Al and X₂ (X = H, F, Cl and Br) (see tables 8-12) and also for AlX₃ products (tables 2-6)

Table 8: Energy quantities (kJmol⁻¹) E₀ at the CCSD(T)/6-311G(d,p)/B3LYP/6-311G(d,p) level of theory, U°, H°, G°, entropy (JK⁻¹.mol⁻¹) S° at the B3LYP/6-311G(d,p) level of theory of aluminum Al in [300K, 1200K] temperature range

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E₀ (kJmol⁻¹)	-	-	-	-	-	-	-	-	-	-
U° (kJmol⁻¹)	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵	6.35×10 ⁵
H° (kJmol⁻¹)	3.72	4.99	6.24	7.48	8.73	9.98	11.22	12.47	13.72	14.97
G° (kJmol⁻¹)	6.20	8.32	10.39	12.47	14.55	16.63	18.71	20.79	22.87	24.94
S° (JK⁻¹.mol⁻¹)	-40.20	-56.37	-72.79	-89.61	-106.79	-124.27	-142.01	-159.92	-178.15	-195.58
	155.61	161.72	166.35	170.14	173.35	176.12	176.99	180.76	182.74	184.55

Table 9: Energy quantities (kJmol⁻¹) E₀ at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, U°, H°, G°, entropy (JK⁻¹.mol⁻¹) S° at the B3LYP/6-311G(d,p) level of theory of aluminum H₂ in [300K , 1200K] temperature range

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E ₀ (kJmol ⁻¹)	-3017.27	-3017.27	-3017.27	-3017.27	-3017.27	-3017.27	-3017.27	-3017.27	-3017.27	-3017.27
U° (kJmol ⁻¹)	48.32	50.44	52.52	54.59	56.67	58.75	60.83	62.91	65.00	67.08
H° (kJmol ⁻¹)	50.80	53.76	56.67	59.58	62.49	65.40	68.31	71.23	74.14	77.06
G° (kJmol ⁻¹)	13.02	-0.34	-14.20	-28.66	-43.59	-58.94	-74.66	-90.70	-107.04	-123.64
S° (JK ⁻¹ .mol ⁻¹)	126.71	135.26	141.75	147.06	151.54	155.43	158.86	161.93	164.71	167.25

Table 10: Energy quantities (kJmol⁻¹) E₀ at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, U°, H°, G°, entropy (JK⁻¹.mol⁻¹) S° at the B3LYP/6-311G(d,p) level of theory of molecular fluoride F₂ in [300K , 1200K] temperature range

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E ₀ (kJmol ⁻¹)	-	-	-	-	-	-	-	-	-	-
	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵	5.23×10 ⁵
U° (kJmol ⁻¹)	18.44	20.57	22.70	24.89	27.16	29.50	31.91	34.39	36.91	39.49
H° (kJmol ⁻¹)	20.92	23.90	26.86	29.88	32.98	36.15	39.40	42.70	46.06	49.46
G° (kJmol ⁻¹)	-38.33	-59.03	-80.10	-101.78	-123.96	-146.60	-169.64	-193.04	-216.78	-240.82
S° (JK ⁻¹ .mol ⁻¹)	198.71	207.30	213.92	219.43	224.20	228.44	232.25	235.73	238.94	241.90

Table 11: Energy quantities (kJmol⁻¹) E₀ at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, U°, H°, G°, entropy (JK⁻¹.mol⁻¹) S° at the B3LYP/6-311G(d,p) level of theory of molecular chloride Cl₂ in [300K , 1200K] temperature range

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E ₀ (kJmol ⁻¹)	-	-	-	-	-	-	-	-	-	-
	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶	2.41×10 ⁶
U° (kJmol ⁻¹)	10.22	12.85	15.55	18.30	21.10	23.92	26.76	29.62	32.48	35.35
H° (kJmol ⁻¹)	12.70	16.18	19.70	23.29	26.92	30.57	34.24	37.93	41.63	45.33
G° (kJmol ⁻¹)	-53.53	-76.69	-100.31	-124.65	-149.59	-175.06	-200.98	-227.32	-254.02	-281.06
S° (JK ⁻¹ .mol ⁻¹)	222.14	223.17	240.02	246.56	252.16	257.04	261.36	265.24	268.77	271.99

Table 12: Energy quantities (kJmol⁻¹) E₀ at the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level of theory, U°, H°, G°, entropy (JK⁻¹.mol⁻¹) S° at the B3LYP/6-311G(d,p) level of theory of molecular bromide Br₂ in [300K , 1200K] temperature range

T (K)	300	400	500	600	700	800	900	1000	1100	1200
E ₀ (kJmol ⁻¹)	-	-	-	-	-	-	-	-	-	-
	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷	1.35×10 ⁷
U° (kJmol ⁻¹)	9.22	12.05	14.88	17.74	20.61	23.49	26.38	29.27	32.16	35.06
H° (kJmol ⁻¹)	11.70	15.38	19.04	22.73	26.43	30.14	33.86	37.58	41.31	45.04
G° (kJmol ⁻¹)	-61.21	-86.81	-112.27	-139.48	-166.81	-194.67	-222.99	-251.73	-280.84	-310.29
S° (JK ⁻¹ .mol ⁻¹)	244.54	255.45	263.62	270.34	276.05	281.01	285.39	289.39	292.86	296.11

The application of equations (4) and (6) coupled to the data in tables 2-6 and tables 8-12 allows achieving the numerical results grouped in tables 13-16. These tables show that Δ_rU° is constant in the case of AlH₃ but varies weakly when it is aluminum halide AlX₃ (X=F, Cl and Br). The absolute values of this variation are 17.98 kJ.mol⁻¹ (AlF₃), 15.48 kJ.mol⁻¹ (AlCl₃) and 15.52 kJ.mol⁻¹ (AlBr₃) when T (K) scans the range [300, 1200]. The same is exactly noted for the reaction enthalpy Δ_rH° with the following values: 3.13 kJ.mol⁻¹ (AlH₃), 6.72 kJ.mol⁻¹ (AlF₃), 4.23 kJ.mol⁻¹ (AlCl₃) and 4.27 kJ.mol⁻¹ (AlBr₃). When one is interested in Δ_rG° the reaction Gibbs energy, the variation takes a significant value when T (K) describes the field [300, 1200] as it is shown by the following results 134.2 kJ.mol⁻¹ (AlH₃), 153.31 kJ/mol (AlF₃), 154.13 kJ.mol⁻¹ (AlCl₃) and finally 153.85 kJ.mol⁻¹ (AlBr₃). Comparison of these values provides the aluminum halide AlX₃ (X=F, Cl and Br) have an identical thermochemical behavior which differs from that of alane AlH₃.

Table 13: Internal reaction energy Δ_rU° (kJ/mol), Heat of reaction Δ_rH° (kJ/mol), Free reaction enthalpy Δ_rG° (kJ/mol) and reaction entropy Δ_rS° (J/K.mol) at the B3LYP/6-311G(d,p) level of theory of alane AlH₃ in [300K , 1200K] temperature range

T (K)	300	400	500	600	700	800	900	1000	1100	1200
Δ _r U° (kJmol ⁻¹)	-280.07	-280.75	-280.90	-280.57	-279.83	-278.75	-277.37	-275.75	-273.93	-271.95
Δ _r H° (kJmol ⁻¹)	-283.79	-285.75	-287.13	-288.05	-288.56	-288.72	-288.59	-288.22	-287.65	-286.92
Δ _r G° (kJmol ⁻¹)	-244.24	-228.11	-213.53	-198.72	-183.78	-168.80	-153.81	-138.91	-123.95	-110.04
Δ _r S° (JK ⁻¹ .mol ⁻¹)	-131.82	-144.09	-147.20	-148.89	-149.68	-149.91	-149.75	-149.31	-148.82	-147.40

Table 14: Internal reaction energy $\Delta_r U^\circ$ (kJ/mol), Heat of reaction $\Delta_r H^\circ$ (kJ/mol), Free reaction enthalpy $\Delta_r G^\circ$ (kJ/mol) and reaction entropy $\Delta_r S^\circ$ (J/K.mol) at the B3LYP/6-311G(d,p) level of theory of aluminum trifluoride AlF_3 in temperature range [300K , 1200K]

T (K)	300	400	500	600	700	800	900	1000	1100	1200
$\Delta_r U^\circ$ (kJmol ⁻¹)	-1718.95	-1717.60	-1715.83	-1713.83	-1711.71	-1709.56	-1707.39	-1705.23	-1703.09	-1700.97
$\Delta_r H^\circ$ (kJmol ⁻¹)	-1722.66	-1722.58	-1722.07	-1721.31	-1720.44	-1719.54	-1718.61	-1717.70	-1716.81	-1715.94
$\Delta_r G^\circ$ (kJmol ⁻¹)	-1670.36	-1652.49	-1635.01	-1617.67	-1600.47	-1583.39	-1566.43	-1549.62	-1532.80	-1517.05
$\Delta_r S^\circ$ (JK ⁻¹ mol ⁻¹)	-174.35	-175.25	-174.10	-172.73	-171.39	-170.18	-169.09	-168.08	-167.28	-165.74

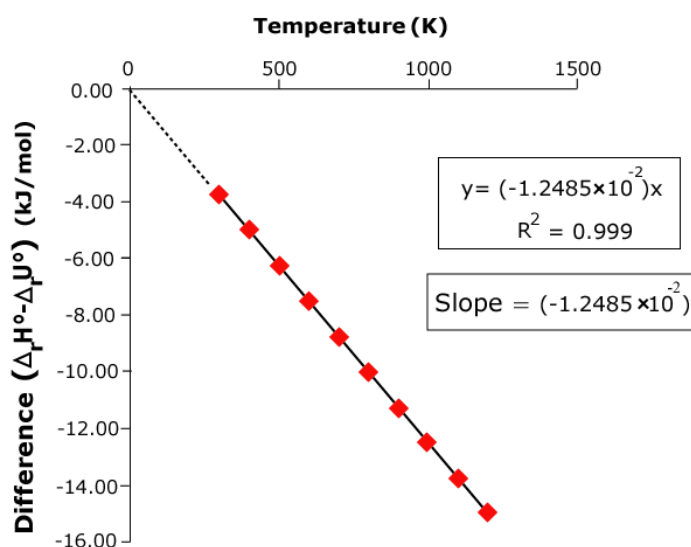
Table 15: Internal reaction energy $\Delta_r U^\circ$ (kJ/mol), Heat of reaction $\Delta_r H^\circ$ (kJ/mol), Free reaction enthalpy $\Delta_r G^\circ$ (kJ/mol) and reaction entropy $\Delta_r S^\circ$ (J/K.mol) at the B3LYP/6-311G(d,p) level of theory of aluminum trichloride $AlCl_3$ in temperature range [300K , 1200K]

T (K)	300	400	500	600	700	800	900	1000	1100	1200
$\Delta_r U^\circ$ (kJmol ⁻¹)	-917.31	-915.84	-914.24	-912.56	-910.83	-909.06	-907.27	-905.47	-903.66	-901.83
$\Delta_r H^\circ$ (kJmol ⁻¹)	-921.03	-920.83	-920.48	-920.04	-919.56	-919.04	-918.50	-917.94	-917.38	-916.80
$\Delta_r G^\circ$ (kJmol ⁻¹)	-868.85	-851.05	-833.64	-816.31	-799.06	-781.88	-764.77	-747.77	-730.72	-714.72
$\Delta_r S^\circ$ (JK ⁻¹ mol ⁻¹)	-173.93	-174.46	-173.69	-172.89	-172.14	-171.45	-170.81	-170.17	-169.69	-168.40

Table 16: Internal reaction energy $\Delta_r U^\circ$ (kJ/mol), Heat of reaction $\Delta_r H^\circ$ (kJ/mol), Free reaction enthalpy $\Delta_r G^\circ$ (kJ/mol) and reaction entropy $\Delta_r S^\circ$ (J/K.mol) at the B3LYP/6-311G(d,p) level of theory of aluminum tribromide $AlBr_3$ in temperature range [300K , 1200K]

T (K)	300	400	500	600	700	800	900	1000	1100	1200
$\Delta_r U^\circ$ (kJmol ⁻¹)	-766.10	-764.61	-763.01	-761.32	-759.58	-757.82	-756.03	-754.23	-752.41	-750.58
$\Delta_r H^\circ$ (kJmol ⁻¹)	-769.82	-769.59	-769.24	-768.80	-768.31	-767.80	-767.25	-766.69	-766.13	-765.55
$\Delta_r G^\circ$ (kJmol ⁻¹)	-717.90	-699.99	-682.64	-665.35	-648.15	-631.02	-613.96	-597.01	-580.00	-564.05
$\Delta_r S^\circ$ (JK ⁻¹ mol ⁻¹)	-173.07	-174.00	-173.21	-172.42	-171.66	-170.97	-170.33	-169.69	-169.21	-167.91

These thermodynamic quantities of reaction, namely the reaction Gibbs free energy $\Delta_r G^\circ$, the reaction entropy $\Delta_r S^\circ$, the difference between reaction enthalpy $\Delta_r H^\circ$ and reaction internal energy $\Delta_r U^\circ$, will be plotted as a function of temperature T to conclude the thermodynamic aspects of the reaction (1) as it is shown in figure 9.

**Figure 9:** Graphical representation of the variation $(\Delta_r H^\circ - \Delta_r U^\circ)$ for different temperatures at B3LYP/6-311G(d,p) level of calculation for the three aluminum halides and alane.

First, Tables 17-20 show that $\Delta_r H^\circ$ (T) and $\Delta_r U^\circ$ (T) are negative for TC [300 K,1200 K] and consequently the reaction (1) is highly exothermic taking into account their high values, which are between $\Delta_r U^\circ$ (1200)=-271.95 kJ.mol⁻¹ for AlH_3 and $\Delta_r U^\circ$ (300)=-1718.95 kJ.mol⁻¹ for AlF_3 , $\Delta_r H^\circ$ (300)=-283.79 kJ.mol⁻¹ for AlH_3 and $\Delta_r H^\circ$ (300)=-1722.66 kJ.mol⁻¹ for AlF_3 . Starting from Al and X_2 (X=H, F, Cl and Br), the reaction (1) can therefore be a relative power source generating a useful Lewis acid AlX_3 . The differences between the values of $\Delta_r H^\circ$ (T) and $\Delta_r U^\circ$ (T) lead, when transformed into graphic representation, to a half-line whose extrapolation substantially passes through the origin. The slope of this straight line coincides with the term:

$$\Delta_r vR = -\frac{3}{2}R = -1.25 \times 10^{-2} \text{ kJ.K}^{-1}.\text{mol}^{-1} \quad (7)$$

R is the gas constant and $\Delta_r v = \sum v$ is the algebraic sum of the stoichiometric numbers of the reaction. For our case, the value of $\Delta_r v$ is (-1.5). This result is consistent with the relationship between the two intensive thermochemical quantities $\Delta_r H^\circ(T)$ and $\Delta_r U^\circ(T)$ according to:

$$\Delta_r H^\circ = \Delta_r U^\circ + \Delta_r (P^\circ V) = \Delta_r U^\circ + \Delta_r v RT \quad (8)$$

Thus, we obtain a diagram that provides the chemical equilibrium curves $\Delta_r G^\circ(T)$ of a set of pairs Acceptor / Donor for which aluminum is the exchanged particle according to the equation:

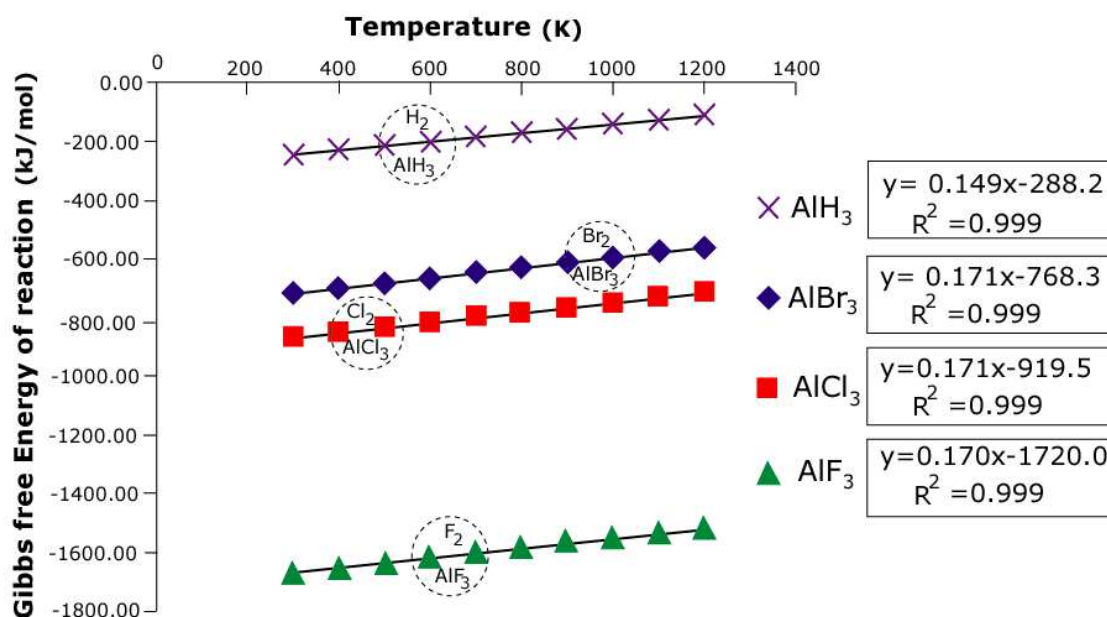
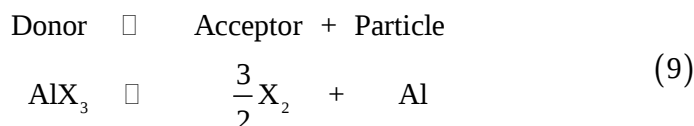
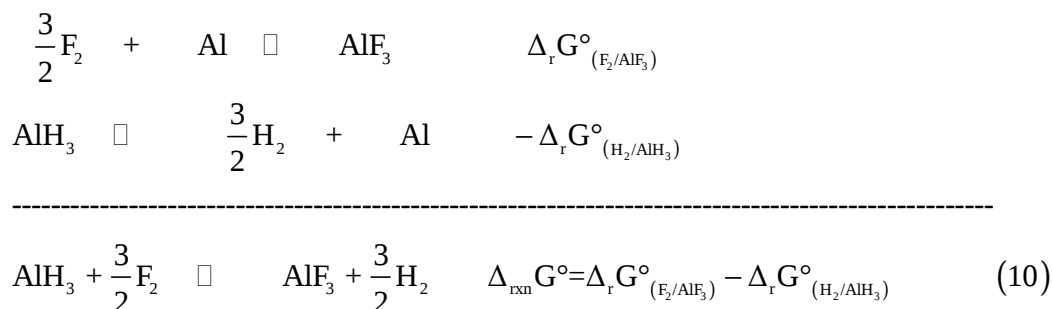


Figure 10: Graphical representation of the Gibbs free energy of reaction for different temperatures at B3LYP/6-311G(d,p) level of calculation for the three aluminum halides and alane.

During these reactions in one way or another the oxidation number (no) of the chemical element X (X=H, F, Cl and Br) changes. Indeed, in X_2 : no (X) = 0, in AlX_3 : no (X) = -1 because aluminum is the least electronegative chemical elements presented in this study. This observation leads to define the oxidizing / reducing couples or pairs as X_2/AlX_3 . Figure 10 indicates that molecular fluoride F_2 is the strongest oxidizing while AlH_3 is the strongest reducing and Cl_2 more oxidant than Br_2 . In other words, molecular fluoride F_2 can oxidize all AlX_3 species whose curves $\Delta_r G^\circ(T)$ are above his and AlH_3 can reduce any X_2 molecule whose curve $\Delta_r G^\circ(T)$ is below hers (figure 10).



$\Delta_{\text{rxn}} G^\circ$ is the free enthalpy of reaction between the two considered couples Ox/Red i.e. H_2/AlH_3 and F_2/AlF_3 . Its T-expression can be deduced from the expressions listed in figure 10.

$$\Delta_{\text{rxn}} G^{\circ}(T) = -1431.1 + 0.021T \quad (\text{kJ/mol}) \quad (11)$$

For any value between 300K and 1200K, this energy $\Delta_{\text{rxn}} G^{\circ}(T)$ is negative and therefore the reaction (10) evolves spontaneously towards the forward direction showing that AlH_3 is the strongest reducing and F_2 strongest oxidant as previously stated.

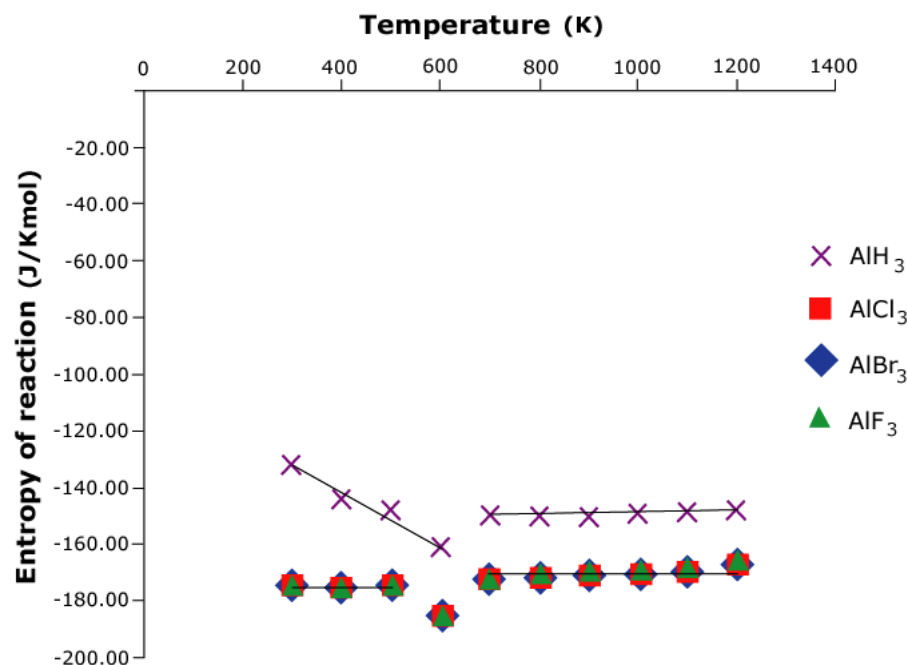


Figure 11: Graphical representation of the entropy of reaction for different temperatures at B3LYP/6-311G(d,p) level of calculation for the three aluminum halides and alane.

In the case of the $\Delta_r S^{\circ}$ reaction entropy, two remarks can be distinguished. Firstly, this quantity has the same value regardless of the element $X = \text{F}$, Cl and Br at any temperature except at $T = 600 \text{ K}$ where there is a break of the curve (figure 11). It is proposed that this singularity may be due to a change of the allotrope one of AlX_3 species during the reaction (second order effect). Secondly, for AlH_3 , $\Delta_r S^{\circ}(T)$ decreases at the beginning to become constant after $T = 600 \text{ K}$: point of singularity. The reaction (1) for AlH_3 reduced the particulate disorder if $T < 600$ but when T exceeds this value; the energy factor outweighs the entropic one.

CONCLUSION

DFT calculations have been carried out to study the temperature effect on alane and aluminium halides AlX_3 ($X = \text{F}$, Cl and Br). We have shown that the thermochemical properties of AlX_3 aluminum halides and AlH_3 alane are sensitive to temperature. Thermochemical properties subject of study in this paper are internal thermal energy U° , enthalpy H° , entropy S° , Gibbs free energy G° in addition to the volumetric heat capacity C_v° at ambient pressure. The electron energy is not influenced by the temperature factor.

The results obtained from calculations performed at B3LYP/6-311G(d,p) level were used to determine the energy quantities relating to the AlX_3 forming reaction starting from H_2 and X_2 . These energetic results show that the reaction studied is, firstly, highly exothermic and also confirm that the thermodynamic stability is in favor of AlF_3 while AlBr_3 is the most stable electronically. Secondly, these results allow us to define acceptor / donor couples type $\text{X}_2 / \text{AlX}_3$ where the particle exchanged is an aluminum atom. These new pairs or couples are arranged on a diagram similar to an Ellingham diagram.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere. The work presented in this article was conducted in *Laboratory of Solar Energy and Medicinal Plants (ENS-Marrakech, Morocco)* by Mustapha Cherkaoui and Mohammed Kouhila. The study concerns 4 Lewis acids. After fixing all the method of calculation and the basis for the development of atomic orbitals, Mustapha Cherkaoui has held two acids AlF_3 and AlCl_3 while Mohammed Kouhila took responsibility for the two others AlH_3 and AlBr_3 . Once the data is collected and transformed into tables by each of us, we both worked for their analysis. Mustapha Cherkaoui has designed data collection tools and managed the transformation of this data into graphs for all the work. Any analysis of the results of this work has been assumed by the two authors Mustapha Cherkaoui and Mohammed Kouhila. The full wording of this article was conducted by Mustapha Cherkaoui and revised by Mohammed Kouhila. All authors declare and approve the final version sent for publication in the JCMMD

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