Canadian Journal of Chemistry
Revue canadienne de chimie

**On the Combustion Heat Originating in Spin Angular
Momentum that Validates the Chemical-Force Theory of
Bonding**

Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2016-0102
Manuscript Type:	Article
Date Submitted by the Author:	13-Mar-2016
Complete List of Authors:	Kidd, R. Garth; University of Western Ontario, Chemistry;
Keyword:	short-lived atomic state, Avogadro Unit, spin angular momentum, chemical-force law, spin-orbit coupling

**On the Combustion Heat Originating in Spin Angular Momentum that Validates
the Chemical-Force Theory of Bonding**

Author: R. Garth Kidd, Department of Chemistry, University of Western Ontario,
London ON, N6A 5B7, Canada.

e-mail: garth@kidd.be Phone: 519-858-2547

Draft

Abstract

Heat generated in combustion reactions, when converted into a vectored force, provides the dynamics for thermo-dynamics. By combining enthalpy data measured calorimetrically with atomization enthalpies coming out of molecular spectroscopy, it is shown here that the heat liberated during a typical hydrocarbon combustion is but the last 25% of the bond-forming potential energy with which free atoms are endowed. In short-lived free atoms this potential energy is manifest as spin angular momentum. This study introduces a new *per-atom* theory of chemical bonding based on the chemical-force law. Codified in this law is the fact that the intra-molecule attractive force exerted by an atom upon its bonded neighbor is directly proportional to the free atom's spin angular momentum, and inversely proportional to the atom's bonded radius. In the context of the other four fundamental forces maintaining structural integrity in material systems, the chemical force is a lot stronger than the gravitational force, stronger than the van der Waals force, weaker than the electromagnetic force, and a lot weaker than the nuclear strong force. Spin-orbit coupling in the heaviest transition-metal atoms enhances the strength of the chemical force. The chemical-force law successfully models per-atom chemical bond strengths throughout the periodic table. It also shows that a horizontal Newtonian force $F = m.a$ originates in atomic spin angular momentum.

Keywords

short-lived atomic state; Avogadro Unit; spin angular momentum; chemical-force law; spin-orbit coupling

Introduction

Ever since a cave-man lit the first fire, humans have known that combustion reactions generate *heat*. This heat when converted into a vectored *force* using a heat engine provides the *dynamics* in thermo-dynamics. But it was only after Antoine Lavoisier in pre-Revolution Paris . . . before he was guillotined during the Reign of Terror . . . had constructed the world's first calorimeter that we have been able to measure exactly *how much* heat is liberated by one chemical unit of fuel. Lavoisier gave the name *caloric* to that heat-producing entity stored in the fuel; today it is called *enthalpy*.

When combustible reactants at room temperature generate products, also at room temperature, they generate heat *isothermally*. Since the enthalpy generating the heat is not present in the fuel as heat but as latent *potential heat*, this raises the obvious question: “What inter-atom force of attraction takes matter from the *atomic state* into the *molecular state* by forming inter-atom chemical bonds; off-loading to surroundings as heat a large amount of bond-forming potential energy in the process?”.

Atomic spectroscopy has revealed that, unlike molecules, short-lived and therefore chemically-active *atoms* are endowed with non-zero *spin angular momentum*; angular momentum that becomes reduced to zero through formation of spin-paired chemical bonds when atomic-state matter becomes chemically-bonded and *molecular*.¹ The purpose of this analysis is to show that the heat generated during a combustion reaction originates *quantitatively* in the spin angular momentum of the atomic precursors to the molecules oxidized and reduced in a combustion reaction. This leads to a new *per-atom* theory of chemical bonding codified in the chemical-force law; a law supporting the conclusion that chemical activity in every molecule is proportional to its per-atom unexpended bond-forming potential.

Newton's Law II codifies the accelerative force $F = m.a$ that causes horizontal motion, but the laws of physics give no indication of where this force originates.² The chemical-force law introduced here now shows that the accelerative force experienced

each time we step on the car's accelerator originates in the spin angular momentum of electrically-neutral carbon atoms, hydrogen atoms, and oxygen atoms.

The energetics of hydrocarbon combustion reactions

Table 1 records, for a wide range of saturated hydrocarbons, the enthalpy increment ΔH transferred from system to surroundings (under standard thermodynamic temperature and pressure; 298 K and 101.3 kPa) when *one mole* of hydrocarbon is burned with the stoichiometric quantity of oxygen needed to ensure complete combustion. The balanced reaction for the 1-C hydrocarbon is $\{\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})\}$ and the atom-count for this chemical system is 9 per hydrocarbon molecule. For the 20-C hydrocarbon the balanced reaction is $\{\text{C}_{20}\text{H}_{42} + 30.5 \text{O}_2(\text{g}) \rightarrow 20 \text{CO}_2(\text{g}) + 21 \text{H}_2\text{O}(\text{l})\}$ and the atom-count for this system is 123 per hydrocarbon molecule (Column 3). Since the atom-count per hydrocarbon, and therefore the physical amount of material under study, increases monotonically with length of carbon chain and size of hydrocarbon molecule, we are not surprised to see that combustion enthalpies recorded on a per-mole basis (*i.e.* on a per-molecule basis in batches of 6.02×10^{23} ; Column 4) also increase uniformly with size of hydrocarbon molecule.³

Table 1. Per-molecule and per-atom combustion enthalpies and atomization energies for saturated hydrocarbons.

Fuel used, 1 mole	Oxygen used, moles	Atom count, AvU	Combustion ΔH , kJ/mol	Combustion ΔH , kJ/AvU	C/H ratio	Product atomization, kJ/AvU	Combustion ΔH over Atomization ΔH
CH ₄ (g)	2	9	891	99	0.25	394	25.1%
C ₂ H ₆ (g)	3.5	15	1560	104	0.33	409	25.5%
C ₃ H ₈ (g)	5	21	2219	106	0.37	415	25.5%
C ₄ H ₁₀ (g)	6.5	27	2878	107	0.40	418	25.5%
C ₅ H ₁₂ (g)	8	33	3509	106	0.42	420	25.3%
C ₆ H ₁₄ (l)	9.5	39	4195	108	0.43	422	25.5%
C ₇ H ₁₆ (l)	11	45	4854	108	0.43	423	25.5%
C ₈ H ₁₈ (l)	12.5	51	5506	108	0.44	424	25.5%
C ₉ H ₂₀ (l)	14	57	6171	108	0.45	424	25.5%
C ₁₀ H ₂₂ (l)	15.5	63	6830	108	0.45	425	25.5%
C ₁₂ H ₂₆ (l)	18.5	75	8085	108	0.46	426	25.3%
C ₂₀ H ₄₂ (l)	30.5	123	13315	108	0.48	427	25.3%

When chemicals are studied macroscopically in molar amounts, the ultimate scientific objective is to understand them *microscopically* . . . scaled down by a factor of 6.02×10^{23} . The objective is to understand the chemical properties of a single molecule in terms of its *atomic* constituents. For this to happen we have to define a new *macroscopic* unit designating *atom-count* in batches of 6.02×10^{23} in the same way that the mole unit designates molecule-count in batches of 6.02×10^{23} . The Avogadro Unit (*AvU*) is here defined as the macroscopic measure of *atom-count* in batches of 6.02×10^{23} ; the conversion factor relating atomic mass units to grams: 6.02×10^{23} amu = 1 g. The relationship between Avogadro Units and mole units is (Atom-count per molecule) = (Avogadro Units) $\div$ (Mole Units); as shown in Column 3. When the per-molecule combustion data is converted into per-atom data in Column 5 using atom-count-per-

molecule, the molecule-size dependence is factored out; and the fundamental aspect of chemical reactions that is atom-specific is dramatically revealed.

The constancy of the per-atom combustion data in Column 5 compared with the per-molecule data in Column 4 tells us there is something *atom-specific* making a reduced carbon atom a superlative heat generator; regardless of the particular molecule in which the carbon atom occurs. As the atom-ratio of carbon in fuel molecules increases towards the value 0.43 (Column 6), the combustion enthalpy rises to a constant value of 108 kJ/AvU for all hydrocarbons. The role of carbon atoms as superb heat generators is confirmed when we look at the combustion data for pure carbon. For the reaction $\{C(s, \text{graphite}) + O_2(g) \rightarrow CO_2(g)\}$, the combustion enthalpy is 131 kJ/AvU; 21% higher than that for the best hydrocarbons. Among all the atoms in the periodic table, reduced carbon is clearly *ne plus ultra* when it comes to generating heat.

The minor enthalpy remnant in atoms that generates combustion heat

A cursory glance at Figure 1 points to a startling new fact. While hydrocarbon combustions are the most explosively dramatic of all chemical reactions, the energy released during a typical combustion reaction is but the last 25% remnant of the bond-forming potential built into the *atomic* elements from which the *reactant* molecules were formed. Column 7 of Table 1 lists the spectroscopically-measured atomization energy of the product carbon dioxide and water molecules in which every combustion reaction terminates.⁴ It is obvious that the dramatic combustion numbers measured calorimetrically (Column 5) are the *last 25%* of the energy off-loaded by atoms when they form carbon dioxide and water directly. The first 75% is off-loaded when the chemical bonds maintaining the temporary stability of *reactant molecules* were formed. The last 25% is off-loaded when the atoms in product molecules become more strongly bonded than they were in reactant molecules. In both cases, the energetic strength of chemical bonds originates in the chemical attractive *force* with which all atoms . . .

carbon atoms in particular . . . are endowed.

Draft

Fig. 1. Enthalpy diagram showing atomization enthalpies for both reactants and products in a combustion reaction. *S*-values show spin angular momentum in $\hbar$ -bar units. (The asterisk designates a short-lived reactive intermediate.)

Every instance of a potential energy difference ΔH , like the ones shown in Figure 1, is generated by a *force*; a *vectored* variable with dimensionality $[M L^1 T^{-2}]$. In this instance it is the inter-atom chemical force F drawing atoms together through distance r during chemical bond formation. During the process of bond formation that converts atoms into molecules the chemical system off-loads to surroundings bonding energy $\Delta H = \int F \cdot dr$; a *scalar* variable with dimensionality $[M L^2 T^{-2}]$ in which magnitude is conserved but direction is not. Figure 1 shows that when carbon atoms, hydrogen atoms, and oxygen atoms draw themselves together under the spontaneous action of the chemical force to form the molecular system $\{CH_4(g) + 2 O_2(g)\}$, the system off-loads to surroundings 2664 kilojoules of heat. This process occurs spontaneously right after atom creation because there is no activation barrier to be overcome.

The off-loading of the last 891 kilojoules (of the original 3555) still remaining in reactant molecules is different; it does not occur spontaneously. Once atoms have formed chemical bonds . . . even weak chemical bonds . . . in the course of becoming molecular, they have created for themselves an activation barrier providing a temporary respite against further chemical activity. If the methane-oxygen mixture in Figure 1 is to off-load its combustion enthalpy of 891 kilojoules, it must first find enough activation energy to break some chemical bonds and regenerate a few free atoms to serve as reactive intermediates; thereby surmounting the activation barrier. This activation energy is provided by the spark that lights the fire. Once this occurs, a chain reaction is set in motion and it continues all the way to a new more-stable equilibrium.

In the two-step process shown in Figure 1 whereby carbon atoms first transform

themselves into methane molecules $\text{CH}_4(\text{g})$ and then into carbon dioxide molecules $\text{CO}_2(\text{g})$, both transformations are mediated by the chemical force F_{Chem} . In the first step, each carbon atom's F_{Chem} draws together, from a distance r of roughly ten molecular diameters, its nearest-neighbor atoms and forms chemical bonds; the length of which determine the molecule's diameter. During this process the atoms off-load the *major* portion of their destabilizing energy $\Delta H = \int F_{\text{Chem}} \cdot dr = 2664 \text{ kJ}$. This major energy off-load allows carbon to become sufficiently stable that it can be stored in a container for future use. In $\text{CH}_4(\text{g})$ the total per-atom bond strength is 333 kJ/AvU ; the atomization energy of one-fifth of a mole of methane.

In the second step, the carbon atom leaves an environment where it is already bonded to hydrogen atoms and enters an environment where it is *even more strongly* bonded. In $\text{CO}_2(\text{g})$ the bond strength is now 536 kJ/AvU ; the atomization energy of one-third of a mole of carbon dioxide. Each carbon(+IV) in $\text{CO}_2(\text{g})$ is 61% more strongly bonded than was the carbon(-IV) precursor in $\text{CH}_4(\text{g})$. In one Avogadro Unit of $\text{CH}_4(\text{g})$ the carbon content is only 20%. In one AvU of $\text{CO}_2(\text{g})$ it is higher by 13 percentage points. In one AvU of $\text{C}(\text{s, graphite})$ whose atomization energy at 717 kJ/AvU is another 33% higher than that for $\text{CO}_2(\text{g})$, the carbon content is 100%. When the task is generating heat, it is carbon atoms that do the heavy lifting thermodynamically.

The chemical force that spontaneously converts atoms into molecules

The attractive force between a positively-charged nucleus and enough negatively-charged electrons to achieve an electrically-neutral particle is the force responsible for the structural integrity of an atom. The strength of this *electromagnetic force* is proportional to the magnitude of the charges that mutually neutralize each other when the exact number of electrons needed to achieve charge neutrality has been bound. The dependence of this specific attractive force F upon positive and negative charges is codified in Coulomb's Law $F = C \cdot (n+) \cdot (n-) / r^2$; where r is the between-charge distance, and C is the electromagnetic proportionality constant. When, for example, a C^+ ion draws unto itself through distance r the 6th electron needed to become an electrically-neutral carbon *atom*,

it off-loads energy $\Delta H = \int F \cdot dr = 1086 \text{ kJ/AvU}$; the first ionization energy of the carbon atom.

Once a carbon atom has achieved charge neutrality however, it is still far from energetically stable. Since the strength of the electromagnetic force is charge-dependent and since the $C^*(at)$ -particle has achieved zero-charge status, the electromagnetic force has exhausted its activity and we must look elsewhere for the new force that has entered the picture; the force that maintains the structural integrity of *all* molecules: homo-nuclear and hetero-nuclear alike; even the 1-atom chemically-interlocked molecules in diamond and graphite.

Figure 1 provides the experimental evidence which identifies that property *specific to atoms* which limits their existence lifetimes as atoms and causes them to become molecular. At the top of Figure 1, atomic-state matter is located several thousand kilojoules higher in energy than molecular-state matter lower down. Figure 1 also identifies the fact that atomic-state matter is characterized by high levels of *spin angular momentum*, whereas molecules lower down have little if any spin angular momentum.

Each *unpaired* electron in the valence shell of an atom contributes one-half an *h-bar* unit of spin angular momentum to the atom. Carbon atoms with 4 unpaired electrons have 2 *h-bar* units of spin angular momentum; the maximum amount for main-group atoms limited to four valence-shell orbitals. Oxygen atoms with 2 unpaired electrons have 1 *h-bar* unit of spin. Hydrogen atoms with 1 unpaired electron have $\frac{1}{2}$ *h-bar* unit of spin. There is only one route by which atoms can off-load their destabilizing potential energy and become stable molecules. It is by forming *spin-paired chemical bonds* and jointly reducing their spin angular momenta, usually to zero; off-loading to surroundings their destabilizing energy as bond energy. The atoms shown at top in Figure 1 reduce their combined spin angular momenta from 8 *h-bar* units to 1 *h-bar* unit when forming combustion reactants; and a further reduction from 1 *h-bar* unit to zero *h-bar* units when forming combustion products.

The two units of spin angular momentum in the molecular system $\{CH_4(g) + 2 O_2(g)\}$ identified here calls for some comment, given that most molecules with an even

number of valence electrons have zero spin. While the oxygen molecule is usually portrayed as $O=O$ with a double bond and zero unpaired electrons, magnetic susceptibility studies reveal that the oxygen molecule is in fact *paramagnetic* with two unpaired electrons and only a *single* $O-O$ bond. This makes the activation barrier in Figure 1 *lower* than normal, and goes a long way towards explaining why molecular oxygen is the strongest naturally-occurring oxidizing agent out there. (This also explains why we cannot survive for more than several minutes without a regular input of atmospheric oxygen.)

The spin angular momentum that generates an atom's chemical force

What is it that makes carbon the best and most readily available heat-producer the world has ever known? (The intra-nucleus strong force that mediates nuclear transmutations is six powers-of-ten stronger than the intra-molecule chemical force that mediates combustion reactions, but it cannot be readily accessed at the local filling station.) To answer this question we must look at $C^*(at)$ in the context of its main-group neighbors in the periodic table. We will see it exerts the strongest attractive force on others because it is the *smallest* atom endowed with the *maximum* spin angular momentum.

Atomization energy measured spectroscopically is the only empirical evidence with which to identify the systematic correlation existing between magnitude of an atom's inherent chemical force F_{Chem} and its position in the periodic table. Once a C^+ ion has become an electrically-neutral but energetically-active $C^*(at)$ atom, its energetic activity is caused not by its charge but by its *spin angular momentum*. Spin angular momentum is quantified in *$\hbar$ -bar units*: Planck's action quantum $h = 6.63 \times 10^{-34} Js$ divided by 2π radians per cycle. An atom's spin angular momentum is measured experimentally using Zeeman-perturbed atomic spectroscopy.⁵

Fig. 2. Atomic-state matter spontaneously becoming molecular-state matter under the organizing activity of spin angular momentum.

Among the main-group elements, it is atoms from the first long row of the periodic table . . . the smallest ones . . . that form the strongest homo-nuclear bonds. And among these it is carbon atoms that form . . . by a wide margin . . . the strongest chemical bonds of all. The atomization energy shown vertically in Figure 2 indicates the *strength* of the force maintaining the chemical integrity of the molecule; and it is clear that the strength of the chemical force in each case is proportional to the spin S of the free atom shown across the top. This experimental evidence validates the *chemical force law* $F_{Chem} = (C_{Chem}/r^4) \times S$; where C_{Chem} designates the chemical force **constant**, S designates the spin angular momentum specific to each free atom, and r designates the inter-nuclear distance upon which the force is inversely dependent. Unlike the long-range electromagnetic force whose separation-dependence varies as $1/r^2$, the chemical force is a *short-range* force whose separation-dependence varies as $1/r^4$.⁶ This short-range r -dependence explains why the smallest atoms form the strongest bonds, and why carbon atoms with the most spin angular momentum form, by a wide margin, the strongest.

Within each row of main-group elements the r -value remains relatively constant along the row, but it gets significantly larger from row to row as we move down the periodic table. When the r -dependence of F_{Chem} is combined with the proportionality constant C_{Chem} we obtain a synthetic constant that is specific to each row of the periodic table. Thus $C_{Chem-Li}$ is the proportionality **constant** specific to Li-row elements as shown in Table 2.

In Table 2 are listed all the homo-nuclear molecules (*i.e.* all the allotropes) formed by the atoms from the Li-row of the periodic table. For Li-row atoms the $C_{Chem-Li}$ value averages 306 kJ per h -bar unit of spin; with a standard deviation of 23%. Here the molecules formed from the extremely electronegative F(*at*) and O(*at*) are outliers; and it has long been known that F₂, O₂ and O₃ are chemically atypical and peculiar, making their bonding uncharacteristically weak, their atomization energies unusually low, and their

oxidative potential energies extraordinarily high. After removing the outliers, the average is $345 \pm 6.6\%$. When any of these molecules is atomized, its $345 \text{ kJ}/h\text{-bar}$ of bonding energy is reconstituted, through $\Delta H = h\nu$, as $h\text{-bar}$ units of spin angular momentum with a spin frequency of 5.4×10^{15} per second.

Draft

Table 2. Atomization energy, atomic spin, and chemical-force constant for Li-row homo-nuclear molecules.

Molecular State		Atomic State	Atomization energy, kJ/AvU	Atomic spin S , $\hbar/2\pi$ units	$C_{\text{Chem-Li}}$ kJ / unit
Li(s)	→	Li(at)	159	0.5	318
Be(s)	→	Be(at)	324	1	324
B(s, <i>amorphous</i>)	→	B(at)	559	1.5	373
B(s, <i>crystalline</i>)	→	B(at)	563	1.5	375
$1/60 \text{ C}_{60}(\text{s}, \text{fullerene})$	→	C(at)	678	2	339
C(s, <i>diamond</i>)	→	C(at)	715	2	358
C(s, <i>graphite</i>)	→	C(at)	717	2	359
$1/2 \text{ N}_2(\text{g})$	→	N(at)	473	1.5	315
$1/2 \text{ O}_2(\text{g})$	→	O(at)	249	1	249
$1/3 \text{ O}_3(\text{g})$	→	O(at)	202	1	202
$1/2 \text{ F}_2(\text{g})$	→	F(at)	79	0.5	158
Average					$306 \pm 23\%$
Average ex. O_2 , O_3 , F_2					$345 \pm 6.6\%$

In subsequent rows of the periodic table another complete shell of electrons has been added to the atom, thereby contributing a significant increase in atomic radius and in molecular inter-atom bond length r_0 . Each of the atoms in the Na-row is roughly 50% larger than its congener in the Li-row. In the K-row each atom is roughly 20% larger than its congener, and in the Rb-row each atom is roughly 15% larger still. Since the strength

of F_{Chem} is inversely dependent on r_0 even as the angular-momentum dependence remains fixed, this means that the value of C_{Chem} is going to decrease incrementally from row to row. Tables 3, 4, and 5 provide the precise values of the row-specific proportionality constant C_{Chem} needed to predict the strengths of the homo-nuclear bonds formed by all the main-group atoms; based on their spin-angular-momentum values.

Table 3. Atomization energy, atomic spin, and chemical-force constant for Na-row homo-nuclear molecules.

Molecular State		Atomic State	Atomization energy, kJ/AvU	Atomic spin S , $h/2\pi$ units	$C_{Chem-Na}$, $kJ / unit$
Na(s)	→	Na(at)	107	0.5	214
Mg(s)	→	Mg(at)	148	1	148
Al(s)	→	Al(at)	326	1.5	217
Si(s)	→	Si(at)	456	2	225
$\frac{1}{4} P_4(s, white)$	→	P(at)	315	1.5	210
P(s, amorphous,	→	P(at)	322	1.5	215
P(s, triclinic, red)	→	P(at)	332	1.5	221
P(s, black)	→	P(at)	354	1.5	236
$\frac{1}{8} S_8(s, yellow)$	→	S(at)	266	1	266
S(s, monoclinic)	→	S(at)	278	1	278
S(s, rhombic)	→	S(at)	279	1	279
$\frac{1}{2} Cl_2(g)$	→	Cl(at)	122	0.5	244

	Average	230 ± 15%
	Average ex. Mg(s)	237 ± 11%

In Table 3 the 148 *kJ* value for Mg(s) is an obvious outlier, and with this outlier removed the average $C_{\text{Chem_Na}}$ value for the Na-row homo-nuclear molecules is 237 *kJ/h-bar*; 31% smaller than the $C_{\text{Chem_Li}}$ value.

Table 4 Atomization energy, atomic spin, and chemical-force constant for K-row homo-nuclear molecules.

Molecular State		Atomic State	Atomization energy, <i>kJ</i>/AvU	Atomic spin <i>S</i>, <i>h</i>/2<i>π</i> units	$C_{\text{Chem-K}}$, <i>kJ</i> / unit
K(<i>s</i>)	→	K(<i>at</i>)	89	0.5	178
Ca(<i>s</i>)	→	Ca(<i>at</i>)	178	1	178
Ga(<i>s</i>)	→	Ga(<i>at</i>)	277	1.5	185
Ge(<i>s</i>)	→	Ge(<i>at</i>)	377	2	189
$\frac{1}{4}$ As ₄ (<i>g</i>)	→	As(<i>at</i>)	267	1.5	178
As(<i>s, cubic</i>)	→	As(<i>at</i>)	288	1.5	192
As(<i>s, amorphous</i>)	→	As(<i>at</i>)	298	1.5	199
As(<i>s, rhombic</i>)	→	As(<i>at</i>)	303	1.5	202
Se(<i>s, red</i>)	→	Se(<i>at</i>)	220	1	220

Se(<i>s, black</i>)	→	Se(<i>at</i>)	227	1	227
$\frac{1}{2}$ Br ₂ (<i>l</i>)	→	Br(<i>at</i>)	112	0.5	224
				Average	197 ± 9.2%

In Table 4 the $C_{\text{Chem-K}}$ value is 17% smaller than the $C_{\text{Chem-Na}}$ value. Also in this Table we can see the small but uniform increase in $C_{\text{Chem-K}}$ value along the row that accompanies the uniform increase in nuclear proton-count causing a uniform decrease in atomic radius. In Table 5 the $C_{\text{Chem-Rb}}$ value is smaller than the $C_{\text{Chem-K}}$ value by 15%.

Draft

Table 5 Atomization energy, atomic spin, and chemical-force constant for Rb-row homo-nuclear molecules.

Molecular State		Atomic State	Atomization energy, kJ/AvU	Atomic spin S , $\hbar/2\pi$ units	$C_{\text{Chem-Rb}}$, kJ / unit
Rb(s)	→	Rb(at)	81	0.5	162
Sr(s)	→	Sr(at)	164	1	164
In(s)	→	In(at)	243	1.5	162
Sn(s, <i>white</i>)	→	Sn(at)	302	2	151
Sn(s, <i>grey</i>)	→	Sn(at)	304	2	152
Sb(s, <i>amorphous</i>)	→	Sb(at)	252	1.5	168
Sb(s, <i>crystalline</i>)	→	Sb(at)	262	1.5	175
Te(s, <i>amorphous</i>)	→	Te(at)	185	1	185
Te(s, <i>hexagonal</i>)	→	Te(at)	197	1	197
$\frac{1}{2} \text{I}_2(\text{g})$	→	I(at)	76	0.5	152
				Average	$167 \pm 8.6\%$

Spin-orbit coupling enhances the chemical force in heavy transition metals

Among the chemically-bonded allotropes formed by the main-group atoms, those of boron and carbon from the Li-row are the only ones with atomization energies of 500 kJ/AvU or greater. And on descending each group from smallest-radius to largest-radius member there is a uniform *decrease* in bond strength, reflecting the $1/r^4$ distance-dependence of the chemical force. In the carbon group, for example, where all five elements have 2 $\hbar$ -bar units of spin, atomization energies decrease from 717 kJ for C(s,

graphite) with a bond length of 154 pm to 195 kJ for Pb(s) with a bond length of 292 pm; 90% greater.

Among the allotropes formed by the transition-metal atoms shown in Figure 3 the dependence of chemical bonding force upon atom size is dramatically different. Of the 27 metals in these nine triads, 14 of them have atomization energies of 500 kJ/AvU or greater. Remarkably, 8 of these 14 occur in the *lowest* row of the periodic table where the bond lengths are *greatest*. And the strongest chemical bonding measured to date . . . in homo-nuclear or hetero-nuclear molecules . . . is the 849 kJ/AvU atomization energy observed in metallic tungsten, W(s). Tungsten is strategically located at the bottom of the *central triad*, where its atomic precursor has the maximum 6 unpaired electrons in a valence shell consisting of six sd^5 hybrid orbitals. And in all but the last two of the transition metal triads, unlike in each of the main periodic groups, the strength of the chemical force *increases* uniformly from upper row to lowest row as *atomic size increases* (Figure 3). When considering the transition metals, a new factor influencing the strength of the chemical force has clearly entered the picture.

This factor is *orbital angular momentum* which gradually augments an atom's spin angular momentum as the atom in the triad gets heavier. As the transition metals within a periodic group get heavier, the interaction between the spin vector and the orbital vector of each valence electron gradually transitions from the Russell-Saunders coupling scheme for the lightest, where orbital momentum makes no contribution, to the j - j coupling scheme for the heaviest where orbital momentum makes its maximum contribution.

Fig. 3. Atomization energies in kJ/AvU for the 1-atom molecules in the nine transition-metal triads, showing increasing orbital enhancement of the spin-dependent chemical force from top to bottom of each triad. Spin plus orbital vector-summed angular momentum for each valence electron is designated by j_i .

Atomic spectroscopists have long known that in the lighter atoms populating the upper rows of the periodic table, the spin angular momentum vector s_i of each valence electron is decoupled from its orbital angular momentum vector l_i .⁷ This means that the spin vector of each unpaired electron couples with the spin vectors of the other unpaired electrons in the valence shell, summing to give the atom's total spin angular momentum S ; the variable that determines the strength of the chemical force F_{Chem} (Figure 2). This pattern of spin-spin coupling is known as the Russell-Saunders coupling scheme and can be represented symbolically by: $(s_1 + s_2 + \text{etc.}) = S$.

However, for heavier atoms populating the lower rows of the periodic table the spin angular momentum vector of each unpaired electron, s_i , is more strongly coupled to its own orbital angular momentum vector, l_i , than it is to another electron's spin vector. The spin vector and the orbital vector *for each electron* sum to give the total angular momentum for that electron, j_i . When the j_i value for each unpaired electron is summed over all the unpaired electrons in the atom's valence shell, this gives the atom's total angular momentum J ; a quantum number that better quantifies the angular momentum in heavier atoms than does S . This pattern of spin-orbit coupling, most pronounced in the lowest transition-metal row of the periodic table, is known as j - j coupling and can be represented symbolically by: $(s_1l_1) + (s_2l_2) + \text{etc.} = j_1 + j_2 + \text{etc.} = J$. Thus, for atoms in the lowest row of the periodic table, J is a better quantum number for predicting the atom's bonding functionality than is S (see Figure 4).

Electrons in s , p , or d orbitals have 0, 1, or 2 units of orbital angular momentum respectively; in addition to their half-unit of spin. Therefore, as spin-orbit coupling becomes stronger, the *total* amount of angular momentum needing to be off-loaded by atomic precursors during bond formation is going to be largest for the heaviest transition metal atoms whose valence electrons located in d -orbitals contain a large orbital component in their total angular momentum. Thus atomic tungsten W(*at*) with 6 unpaired electrons, each of whose spin is augmented by orbital angular momentum, forms the

strongest bonds yet recorded.

In the upper two rows of Figure 3 the fact that V(*at*) and Nb(*at*) form the strongest bonds suggests that the valence-shell electron configuration is pure d^5 and each atom has the maximum for its row of five unpaired electrons. Again, spin-orbit coupling provides Nb(*s*) with stronger bonds than those in V(*s*).

Although orbital augmentation is most strongly manifest among the heavy transition-metal elements, there is a hint of orbital augmentation in Ba(*s*); at the bottom of the alkaline earth group headed by beryllium. Whereas the atomization energies for the alkali metals, each having a single *s*-electron with zero orbital angular momentum, decline uniformly from 159 *kJ* for Li(*s*) to 76 *kJ* for Cs(*s*), the pattern for the alkaline earths is a little different as shown on the left in Figure 3. Here the atomization energies decline uniformly from 324 *kJ* for Be(*s*) to 164 *kJ* for Sr(*s*); but at Ba(*s*) with its 180 *kJ* of atomization energy 10% *higher* than that of Sr(*s*) the decline has turned around. Barium's two unpaired electrons are each in *sd* hybrid orbitals where the large orbital angular momentum contributed by the *d*-fraction is coupled to the electron's spin angular momentum, thereby increasing the strength of the chemical force.

Mercury just to the right of gold in the bottom row of the periodic table (Figure 3 provides another telling example of angular momentum's central role in chemical bonding. With 12 electrons in its valence shell consisting of six sd^5 hybrid orbitals, the mercury atom has zero unpaired electrons and, therefore, *zero angular momentum*. Mercury's 61 *kJ/mol* latent heat of vaporization $\text{Hg}(l) \rightarrow \text{Hg}(g)$, six times lower than gold's atomization energy, suggests that the microscopic particles in liquid mercury are held in contact by the van der Waals force, not by the chemical force. In this respect the microscopic particles of mercury are more akin to those of an inert gas such as Xe(*g*) than to those of the atomic elements.

Fig. 4. Potential energy off-loaded by the heaviest transition metal atoms on becoming

molecular, showing chemical force augmentation due to spin-orbit coupling; and the *ca.* 200 *kJ* atomization energy increase due to the lanthanide contraction.

Figure 4 provides a graphic illustration of how the spin dependence of the chemical force in lowest-row transition metals is substantially enhanced by the orbital contribution to the atom's total angular momentum J shown across the top. The J -value for each atom is calculated in the following way. The valence shell for each of the transition metal atoms, shown in Figure 3, consists of six sd^5 hybrid orbitals. Each orbital is one-sixth s -character and five-sixths d -character. s -character translates into $1/2$ an $\hbar$ -unit of spin angular momentum per unpaired electron, and d -character translates into $2 \hbar$ units of orbital angular momentum per electron. Therefore, each unpaired electron in an sd^5 hybrid orbital contributes $(1/6 \times 1/2) + (5/6 \times 2) = 1.75 \hbar$ units to total angular momentum J .

Figure 4 also shows the *ca.* 200 *kJ* effect on atomization energies of the *lanthanide contraction*. Sequentially in the periodic table between lanthanum and hafnium there are 14 lanthanide elements, each contributing the positive charge of an additional nuclear proton. As a result, the bonded radius of metal atom goes from 188 *pm* for La(s) to 159 *pm* for Hf(s); a contraction of 15%. The largest per-element contraction the rest of the way from Hf(s) to Au(s) is only 4%. This is the same per-element contraction as occurs in each of the upper rows. Thus all the elements between hafnium and gold have radii 15% smaller than they would have been were it not for the lanthanide contraction. This 15% size reduction adds roughly 200 *kJ* to their atomization energies making these transition metals among the most strongly bonded of all substances.

The angular-momentum theory of chemical bonding

Figure 2 above presents for the first time the experimental evidence upon which a radically new theory of chemical bonding has been built. This new theory is radical in that it is founded on a new fundamental *force*; the chemical force that has not previously been

characterized.

Already characterized quantitatively are four fundamental forces, operating to maintain the structural integrity of categorially-distinct material entities. Listed from weakest to strongest they are:

- (i) the mass-activated *gravitational* force maintaining the structural integrity of the Solar System, characterized by Isaac Newton in the 1670s.
- (ii) the polarity-activated *van der Waals* force maintaining the contiguity of discrete (*i.e.* non-interlocked) molecules in the liquid state, characterized by Diderik van der Waals in the 1870s.
- (iii) the charge-activated *electromagnetic* force maintaining the structural integrity of atoms, characterized by Charles Coulomb in the 1780s.
- (iv) the hadron-activated *strong force* maintaining the neutron-proton structural integrity of atomic nuclei, placed at the core of the Standard Model by several physicists in the 1960s and 1970s.

Into the middle of this hierarchy of forces, a new fundamental force has now been inserted, as shown in Figure 5.

Fig. 5. The five universal attractions maintaining structural integrity in physical and chemical systems at the microscopic, macroscopic, and cosmic levels.

Stronger than the van der Waals inter-molecule force and weaker than the electromagnetic force binding core electrons to an atomic nucleus so strongly they take no direct part in the chemical activity of atoms, we find the chemical force that maintains the structural integrity and chemical characteristics of a molecule. The chemical force is activated by each atom's spin angular momentum and this dependence is codified in the

chemical force law $F_{Chem} = (C_{Chem}/r^4) \times S$. Here the S -variable designates the spin angular momentum specific to each atom, and C_{Chem} designates the value of the generic chemical force **constant**.

Fig. 6. The chemical-force law modeling the per-atom bond strength in the hydrogen molecule.

The hydrogen atom at 37 pm has the smallest covalent radius among all the atoms in the periodic table. Since the row-specific average atomic radius *increases* incrementally row-by-row on moving down the periodic table, Figure 6 shows that the single-atom H-row has the highest row-specific chemical-force proportionality constant: $C_{Chem-H} = 436$ kJ/h-bar. The inter-nuclear distance r remains relatively constant along each of the lower main-group rows of the periodic table. When this r -dependence is factored into the proportionality constant, we get values that remain constant within each row but which diminish with increasing r from row to row. These values are: $C_{Chem-H} = 436$ kJ/h-bar, $C_{Chem-Li} = 345$ kJ/h-bar, $C_{Chem-Na} = 237$ kJ/h-bar, $C_{Chem-K} = 197$ kJ/h-bar, and $C_{Chem-Rb} = 167$ kJ/h-bar.

Once the proportionality constant $C_{Chem-Li}$ has been evaluated (Table 2), this new bonding theory allows one to predict that carbon atoms . . . among all the main-group elements . . . will form the strongest chemical bonds. One can also understand why the bonding in Be(s), B(s), and C(s, *graphite*) is approximately 2×, 3×, and 4× stronger than the bonding in Li(s). Neither the valence-bond theory nor the molecular-orbital theory provides this degree of insight into the factors that determine chemical bond strengths and, therefore, heats of combustion.

Bonding theories presented in chemistry textbooks appearing since *The Nature of the Chemical Bond* was published in 1939 fail to provide even a rough estimate of the

strength of the *generic* chemical bond.⁸ Why? The answer is very simple. While both the valence bond and molecular orbital theories have been moderately successful at modeling the bonds in the smallest diatomic molecules, the orbital overlap calculation only succeeds *after the inter-nuclear bond-length is already known*. Neither model contains a variable specific to each atom that will quantify the strength of the attractive force that draws atoms together into this bonded configuration. Since the overlap integral can only be calculated once the inter-nuclear distance is known, there is a teleological element to the overlap calculation; and scientists have traditionally eschewed teleological causes.

The only attractive force featured in the conventional bonding theories is the electromagnetic force between a positive nucleus and negative electrons. And while this force is the sole determinant of atom integrity, it makes zero contribution to the force that draws atom to atom during molecule formation. Nowhere in the valence bond theory nor in the molecular orbital theory is there any identification of the atom-specific spin angular momentum that activates atoms and causes them to be short-lived particles which spontaneously become molecular through chemical-bond formation.

Perhaps the reason the chemical force specific to atoms has not previously been identified can be attributed to a categorizing error present in NBS (and now NIST) compilations of chemical thermodynamic data. There, all bond-free atoms are given the misleading (g) designation which assigns them to the *gas* category of matter. Unlike genuine gases . . . He(g), H₂(g), N₂(g), O₂(g), Cl₂(g), for example . . . all of which have zero spin and all of which are identified as gases because they adhere closely to the gas equation $P.V = n.R.T$ where sample volume is directly proportional to *molecule count* (regardless of atom-count per molecule); none of H*(at), N*(at), O*(at), Cl*(at) comes even close to obeying the gas law.

Molecules in the liquid state . . . He(l), H₂(l), N₂(l), O₂(l), Cl₂(l) for example . . . are designated as such with the (l) symbol. The same molecules in the gaseous state . . . He(g), H₂(g), N₂(g), O₂(g), Cl₂(g) . . . are clearly differentiated from their liquid counterparts

with the (g) symbol. When the enthalpy input causing the *isothermal* phase transition $\text{H}_2(l) \rightarrow \text{H}_2(g)$ is measured and found to have the value 0.904 kJ/mol , this ΔH increment is called “the latent heat of vaporization”, and its activity at the microscopic level can be recognized as causing a separation of molecules one from another against the van der Waals force of attraction; resulting in a *ca.* 1400-fold increase in volume.

When the much larger latent heat of *atomization* $\Delta H = 436 \text{ kJ/mol}$ causing the *isothermal* atomization of molecular hydrogen $\text{H}_2(g) \rightarrow 2 \text{ H}^*(at)$ is not explicitly labeled with the (at) symbol, but remains as presently depicted . . . $\text{H}_2(g) \rightarrow 2 \text{ H}(g)$. . . in NBS and NIST compilations of thermodynamic data, the huge energetic difference between an electrically-neutral but highly energized *atom* and a gaseous molecule such as $\text{H}_2(g)$ will continue to be overlooked. Without a designation change from $\text{H}(g)$ to $\text{H}(at)$, the powerful activity of the chemical attractive force with which *atoms* are endowed will continue to be masked behind the misleading (g) symbol that assigns short-lived, highly-reactive, bond-free atoms to the wrong existential category.

The atom *is* the elementary particle of chemistry. But it is energetically unstable and . . . on its own . . . devoid of *chemical* properties: acidity, basicity, oxidizing strength, reducing strength, *etc.* Chemical properties are *emergent* properties; they emerge during the spontaneous formation of chemical bonds, as atoms off-load their destabilizing energy while becoming molecular. And contrary to what we are told in chemistry textbooks and dictionaries, the *smallest* particle of any substance . . . homo-nuclear ‘element’ or hetero-nuclear ‘compound’ . . . is in fact *the molecule*.

References

- (1) Herzberg, G. *Atomic Spectra and Atomic Structure*; Prentice-Hall: 1937; reprinted Dover: New York, 1944, pp. 128-135.
- (2) Newton, I. *Philosophiæ Naturalis Principia Mathematica*; London, 1687; tr.

- Cohen, I. B. and Whitman, A. *The Principia*; University of California Press: Berkeley, 1999, p. 416.
- (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* (Supplement 2), 1.
- (4) Gaydon, A. G. *Dissociation Energies and Spectra of Diatomic Molecules*; Chapman & Hall: London, 1968.
- (5) Herzberg, G. *Atomic Spectra and Atomic Structure*; Prentice-Hall: 1937; reprinted Dover: New York, 1944, p. 96.
- (6) Kidd, R. G. *Found. Chem.* **2011**, *13*, 109.
- (7) Herzberg, G. *Atomic Spectra and Atomic Structure*; Prentice-Hall: 1937; reprinted Dover: New York, 1944, p. 174.
- (8) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, 1939.