

DOI: 10.1002/cphc.201000330

Segregation into Layers: A General Problem for Structural Instability under Pressure, Exemplified by SnH₄

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When a molecular compound is thermodynamically unstable (but kinetically persistent) with respect to the elements, structures that contain segregated layers of the elements may be favored at moderate pressures, as a compromise between the potential stability of novel electronic configurations and decomposition into the elements (or other stable compounds). We use stannane, SnH₄, to approach this quite general problem theoretically, since the heat of formation of SnH₄ is so positive. Our ground-state DFT searches for optimal structures

begin with slabs formed from 1–4 layers of tin atoms in the β -Sn and bcc configurations, and also slabs of molecular hydrogen or hydrogen atoms, preserving the overall SnH₄ stoichiometry. As argued, segregated layers are an important structural feature in the lower- and moderate-pressure regime (0 and 50 GPa). By 140 GPa ($V/V_0=0.21$) the coordination of tin and hydrogen increases and the slabs disappear, as judged from the optimized structures.

1. The Question As It Emerges for SnH₄

We (and others) have been looking theoretically at the structures under pressure of group 14 tetrahydrides.^[1–12] The motivation for examining just this group of compounds is the idea of “chemical precompression”.^[13] Given the difficulty of metalizing molecular H₂^[14,15] (a potential superconductor and superfluid),^[13,16,17] the core concept is that the effective repulsion between hydrogen molecules might be reduced in [H₂A] by the hydrogen atoms bonding to other atoms [A].^[15–17]

The general problem of segregation that we expose herein arose from some very specific considerations of the geometrical and electronic structure of SnH₄ under pressure. Our studies began with some trial structures based on previous experiments and extensive theoretical work on SiH₄, GeH₄, and SnH₄. The red line in Figure 1 shows the calculated enthalpy of the most stable structure for SnH₄ that we have reached in this exploration. The reference [0] enthalpy line in this graph is the enthalpy of Sn + 2H₂, computed for the most stable structures of the separated elements at a given pressure (Sn evolves from

diamond α -Sn, to β -Sn, to bct, to bcc; while H₂ evolves from P6₃/m, to C2/c, to Cmca-12).^[18,19] The trial structures we explored (and the excursions in the enthalpy vs pressure curves that hint at phase transitions) are of substantial interest, and they will be discussed in detail elsewhere.^[20] Herein we focus, however, on the fact that over a wide pressure range (~180 GPa) the separated elements (blue reference line) may be more stable.

Why do we say “may” and not “are”? Because there is an enthalpic penalty (for Sn, not so much for H₂) for “cutting” such layers out of the solid. In forming layers of Sn (at 1 atm of higher pressures) one has created a chemically reactive slab—it has low-lying unfilled and high-lying filled orbitals. Such a slab will effectively bond to the H₂ layer, a stabilizing interaction. The new interlayer bonding potentially compensates for this intralayer penalty. But we do not imagine that it will fully do so.

This simple realization puts a new perspective on the search for optimal structures in this low- and medium-pressure regime. As we will see, a systematic search in fact finds some layered structures falling in enthalpy between the continuous curve in Figure 1 and those of the separated elements. In quite independent work, a similar trend toward layered structures

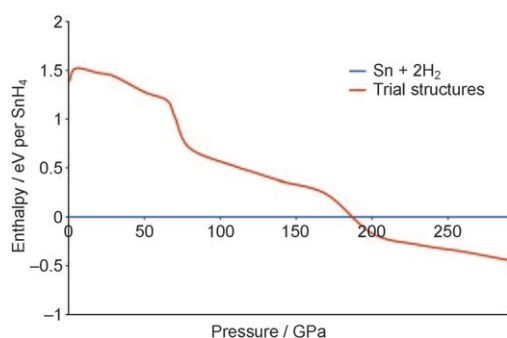


Figure 1. Computed relative enthalpies per formula unit of hypothetical SnH₄ structures as a function of pressure. The zero of enthalpy corresponds to the stable form of the elements, Sn + 2H₂, at the given pressure.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/cphc.201000330>.

has been seen theoretically, in silane^[4] and germane,^[7] and just recently, stannane, and plumbane,^[21] and Gao and coworkers concluded that segregation is also likely in pressurized stannane at $P < 96$ GPa.^[22]

2. The General Problem of Segregation

The favoring of slabs is not surprising when we take a look at the formation energy (ΔH_f°) of the group 14 hydrides. Of these hydrides, only CH_4 has a negative heat of formation, ΔH_f° . A molecule of stannane (and so, approximately, the $P=1$ atm solid), with an experimental heat of formation of $+1.68$ eV/ SnH_4 molecule,^[23] is thermodynamically unstable, yet kinetically reasonably persistent (at 298 K). Gaseous stannane in fact slowly decomposes to the elements at $P=1$ atm.^[24]

The problem presented by a system under pressure segregating into its elements—if there is a thermodynamic driving force for the reaction—is a very general one. It faces experimentalists in the area continually, but (for reasons of avoiding complexity, we think) has not received sufficient attention from the theoretical community. This motivates, in part, the present paper.

Many interesting questions arise as one begins to think of segregation. Among them: If segregation to atom slabs is favored, how many layers will there be in each slab? Is a specific ordering of (in our case) tin atoms preferred within a slab? Can this ordering be predicted from our knowledge of existing tin allotropes at high pressure? Will the hydrogen atoms, within a layered structure, always prefer to form molecular pairs? What about their orientations? At what pressure does the formation of a novel three-dimensional tin-hydrogen bonding framework become favored over segregation of the elements?

We address these questions specifically for SnH_4 below. We use reasonably standard DFT computational methodology in these explorations; the details are provided in the next section. Following the present experimental impetus, our main focus is on the manifestations of the pressure variable, P , recognizing however that the temperature variable, T , and associated entropic effects may also be of considerable importance. The atoms are also taken as static, a matter on which we comment later.

We restricted ourselves to computations to four formula units in a unit cell ($Z=4$). If a substance “wants” to segregate, this limitation favors not especially thick layers, and so potentially an incomplete expression of the tendency to segregate. Nevertheless, we are confident that the driving force for segregation notably manifests itself even within a relatively small unit cell.

Computational Methodology

In our computations we made use of density functional theory (DFT) with the Perdew–Wang exchange–correlation functional^[25] with Blöchl’s projector-augmented wave method (PAW) and a plane wave basis set, as implemented in the Vienna ab initio simulation package (VASP) codes. For tin, 5s and 5p were treated as valence states.

For the optimization of the structures, the cell parameters, the atomic positions, and the cell volume were all allowed to relax. The stress tensor was also calculated. A defined stress was added to the stress tensor, converging to a particular pressure. Once an optimized structure was reached, the electronic density of states per electron (DOS) was calculated. The k -point grids were generated via the Monkhorst–Pack scheme.^[26] The calculations are for the ground state at 0 K, and as noted neglect the zero-point vibrational energy. The cutoff of the kinetic energy was set at 650 eV, and for the planewaves we set a self-consistent field (SCF) tolerance of 1×10^{-5} eV/unit cell. Wigner–Seitz radii were oriented along the atomic radii given in the PAW potentials: $r(\text{Sn})=1.566$ Å, $r(\text{H})=0.37$ Å.

The structures were optimized at pressures of 0, 50 and 140 GPa. Indeed, calculations where the tin slab was taken from the β allotrope proved prohibitive after two layers, that is, with a $Z=4$. In other cases, the energies were so high after the first optimization that we no longer considered them as likely SnH_4 structures.

3. Preparing Segregated or Layered Structures for Calculation

We started by first setting up layered structures preserving the bulk SnH_4 stoichiometry, to see if they would optimize to structures closer to the separated elements than the parent compound. In this preparation process we focused mainly on the slabs of tin atoms, our rationale being that Sn–Sn interactions carry greater consequences for the enthalpy than the weaker H_2 – H_2 interactions, at least at relatively low pressures where distinct H_2 molecules are likely to be seen.

Within a slab of tin atoms, our starting structures contained 1–4 layers. The number of layers is in some way arbitrary, since two layers can easily merge into one. So Z , the total number of formula units (SnH_4) within a unit cell, is also specified. Tin itself changes phases as pressure is applied^[18] at moderate temperatures: α -tin is stable at very low pressures, readily transforming to β -tin, which is energetically more favorable from just above atmospheric pressure to ~ 10 GPa. At higher pressure pure tin undergoes a phase change to bct and at 44 GPa takes on the bcc structure.^[18] We focused our attention on the structures that are most stable over a wide range of pressures, namely β -tin in the low-pressure regime and bcc at high pressures. For the sake of simplicity, we select one crystal plane per Sn allotrope and then form slabs of varying thickness around that plane. Examples are shown in Figure 2.

What about possible hydrogen slabs? We knew from preliminary work on high-pressure phases of SnH_4 that in some of

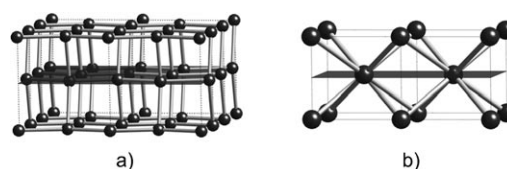


Figure 2. The Sn elemental structure planes around which further layers were taken to form Sn slabs in trial structures. The reference planes are depicted in gray. a) β -Sn structure, b) bcc Sn, the most stable structure for bulk tin at high pressures.

them H_2 pairs do persist, while in others the H–H bond is broken. We wished to give the system an optimal chance to locate both kinds of structures, and to introduce Sn–H interactions as needed. This led us to start out with two kinds of structures for each hydrogen slab: in one of them we placed dihydrogen molecules at different position in between two slabs of tin. In the other initial geometry choice, atoms (rather than molecules) of hydrogen are placed in layers, loosely following a basis in a simple tetragonal Bravais lattice. Figure 3 shows an illustrative example of these two starting points.

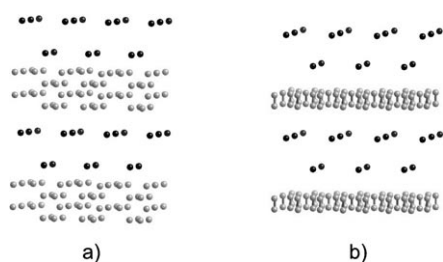


Figure 3. Two different starting points for slab optimizations. (Sn = black, H = light gray). a) Hydrogen atoms are placed in this structure, but not paired; b) All hydrogen atoms are paired.

Putting the slabs together, we then come to the starting structures for our enthalpy optimization. (The Supporting Information, to this paper, in Figure S1 shows several such arrangements, for the “undimerized” hydrogen atom starting point.) In these initial geometries we kept $H-H \geq 1.2$ Å. There may be incipient H–H bonding even at 1.2 Å; there are (a few) molecular H_2 complexes known with that distance, and they indeed show some sign of bonding.^[27–30] We also left some additional space among hydrogen and tin atoms (~2 Å) in our starting structures for both cases; the Sn–H bond distance in a tin tetrahydride molecule at one atmosphere is 1.7 Å. The general idea was to start optimizations with structures that allow hydrogens to bond or not bond with each other, and with the tin layer as determined by enthalpy minimization.

4. SnH_4 Layers at One Atmosphere Pressure: Geometry.

In our calculations the most stable layered system at 1 atm emerges from optimizing a starting structure of tin atoms in a slab of two bcc layers alternating with an array of initially unpaired hydrogen atoms, and with $Z=4$. As seen in Figure 4a, the hydrogen atoms do pair in the course of this optimization. A layered structure derived from a starting point with paired hydrogen atoms has a slightly higher enthalpy (by 0.21 eV/ SnH_4). The final structure in that case has a similar ordering within the tin layer, but the axes of the hydrogen molecules assume an average orientation that follows the corrugations of the tin layer. It is not surprising that several structural options are then found for the hydrogen layer, differing in H_2 orientation; at low pressure, for nonmetallic arrangements, small dispersion forces (van der Waals bonding) determine the ordering

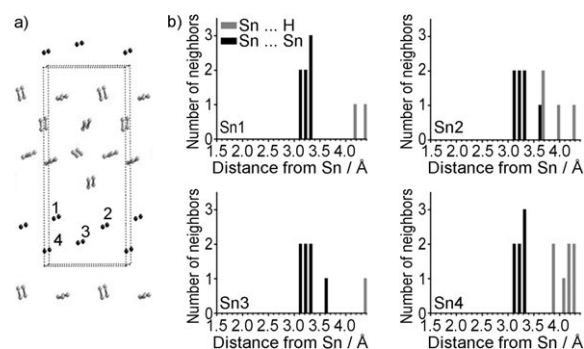


Figure 4. The most stable layered ground-state structure for tin tetrahydride, at 0 GPa, and the coordination environment of the Sn atoms in it. a) A unit cell embedded in a larger view of the layered system. There are four different types of tin locations (numbered). Each has a distinct coordination environment. b) The coordination of each tin atom is shown in portions of distance histograms (in gray, distances from the reference Sn atom to hydrogen; in black, to tin).

of H_2 molecules in their own layer. Also local approximations to DFT functionals generally do not give dispersion forces reliably.

There are four different types of tin locations in the optimized $Z=4$ structure. A useful way to gain insight into the geometrics of bonding in an extended structure is to construct histograms of the calculated atom separations, which we do in Figure 4b. As these diagrams show, each Sn (numbered in Figure 4a) has a distinct coordination environment. Note the Sn–Sn separations lying between 3.0 and 3.6 Å, similar to those in α -tin (3.02 Å) and β -tin (2.8 and 3.1 Å). The Sn–H distances are long (the shortest is ~3.7 Å, longer by far than the normal Sn–H bond length in stannane (1.7 Å)). It is clear that in this layered structure there is little manifestation of the Sn–H interaction and just some small reconstruction in the Sn layers. This structure is very different from the molecular crystal system which first comes to mind when we think about SnH_4 .

One more point on Sn/H interfaces merits mention. Contemporary surface science has provided us with much information on metal and semiconductor surfaces, and their interaction with molecules.^[31] Most of such experimental studies are made, however, under high-vacuum conditions. We have looked at the somewhat sparse literature on tin surfaces and this is summarized in the Supporting Information. Briefly, there is little structural information on α - and β -Sn surfaces.

5. Energetics and Enthalpics of Layering at $P=1$ atm

What is the “energetic price” that the layered structure has to pay for the arrangement we have found? Using the enthalpies of the most stable allotrope of tin and of molecular hydrogen at 1 atm pressure as a reference, our optimized layered structure is unstable by +0.37 eV per SnH_4 .

Let us see if we can take apart the contributions to the enthalpy of the optimum layered structure. We calculate that to excerpt a β -tin layer from the elemental structure costs

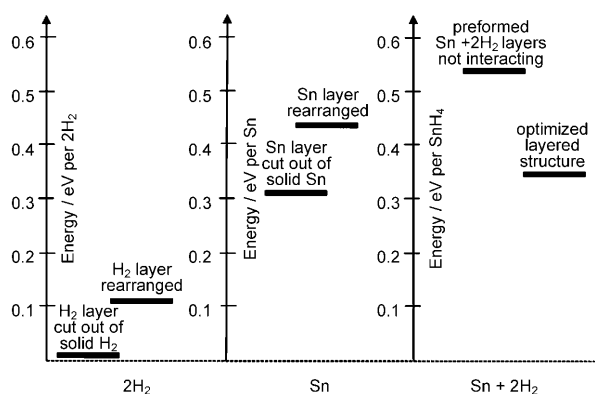


Figure 5. Energetics for the tin tetrahydride layered structure. The zero of energy for the right side of the Figure is the sum of the energies of the separated β -tin and 2H_2 structures (eV per SnH_4); on the left the zero of energy is of individual Sn or 2H_2 , as appropriate (eV per Sn or eV per H_2 accordingly). “Rearranged” means Sn and 2H_2 layers taking on the geometry they take up in the optimized layered structure.

+0.31 eVatom⁻¹. To cut out 2H_2 from its elemental structure costs much less (since only dispersion forces are involved in the process), namely +0.03 eV per atom. Figure 5 shows these energies at its left. To rearrange an isolated β -tin layer to the geometry it has in the optimized layer structure costs 0.10 eV more (a total of +0.43 eV), to rearrange the H_2 layer the cost is +0.11 eV. Bringing the preformed Sn and H_2 layers together is therefore a stabilizing process, by -0.17 eV per H_2 . These components of the energy are shown graphically in Figure 5. The general picture holds—it costs energy to cut out slabs of Sn and H_2 from their solids, that penalty is compensated in part by Sn– H_2 interactions.

We expect that if we took thicker slabs for Sn and H_2 (higher Z) the enthalpy of the slabs would approach that of the elements, the blue reference line in Figure 1.

6. Electronic Structure of the Layered Material at $P=1$ atm

The computed structure can be described as $\text{Sn}(\text{layer})\cdot 2\text{H}_2$. What one might expect in its electronic structure are prominent molecular σ_g and σ_u^* derived bands for the H_2 layer, but slightly broadened. The Sn layers are rather thin (but dense within the layers themselves), and we anticipate them to be metallic, a substantial density of states (DOS) at the Fermi level arising from the “dangling bonds” of the Sn slab carved out of its bulk structure (the next section describes experimental and theoretical work on related Sn surfaces).

Figure 6 shows the density of states (DOS) per electron of the $P=1$ atm $\text{Sn}(\text{layer})\cdot 2\text{H}_2$ arrangement, and the contribution of the Sn and H atoms to that DOS. For this average density the Wigner–Seitz radius, r_s value is 2.67 ($a_0[(4\pi/3)r_s^3 a_0^3 V/N_e]$).

The structure is indeed distinctly metallic. An analysis of the contributions of various atomic states to the total DOS (see the Supporting Information) shows that H_2 σ_g contributes much of the DOS peak at -6 eV, overlapping a region of mainly Sn s states. The layer like structure should show up in a

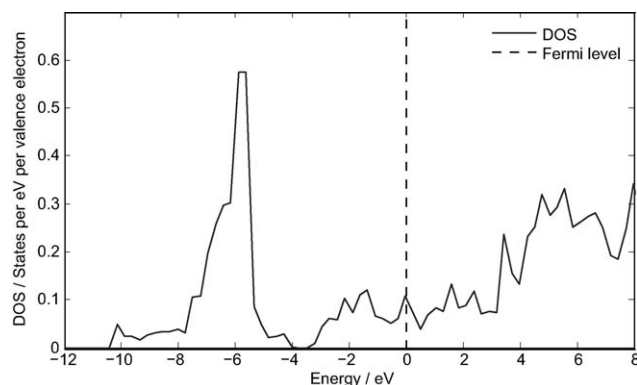


Figure 6. Density of states plot for SnH_4 at 0 GPa, $Z=4$, nominal $r_s=2.67$.

characteristic rectangular DOS feature at the low-energy side of the DOS. One sees only a trace of such behavior.

7. 50 GPa Structures ($V/V_0=0.32$)

Moving from 0 GPa to 50 GPa, the volume of the unit cell decreases, prompting shorter distances between elemental layers. The starting point for the lowest enthalpy structure computed at 50 GPa, (and again, $Z=4$) has the tin atoms cut out of slabs of β -Sn. The final ordering of the tin atoms within the slab is, however, different from β -tin. The hydrogen molecules in this structure have a calculated H–H separation of 0.79 Å, slightly longer than gas phase H_2 separation at 0.74 Å. The H_2 axes are noticeably aligned, as Figure 7a shows. The average orientation of the slab of H_2 diatomics seems to “follow” the way the tin layer folds. We did not study the energetics of further displacement of the H_2 molecules in their sublattice, or their rotational and orientational characteristics. It is likely that even at 50 GPa the barriers to displacement in the H_2 sublattice are small, and given the inadequacy of our functional for dispersion interactions, we did not explore such motions. Gao et al. obtained similar-looking structures at 50 GPa, using an evolutionary algorithm structure search.^[22]

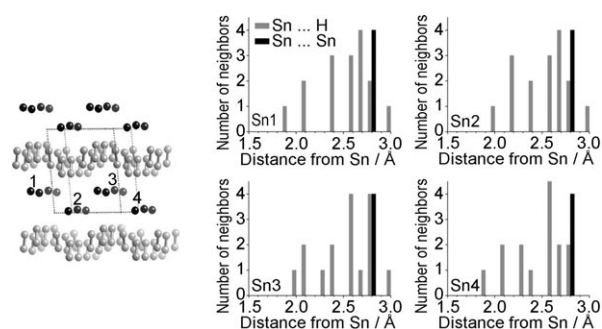


Figure 7. The lowest enthalpy structure for SnH_4 computed at 50 GPa and its associated tin coordination environment. a) The unit cell of the optimized system, extended in this view beyond the unit cell (----). There are four different types of tin atoms, each with a distinct coordination environment (numbered). b) Portions of distance histograms for the different tin atoms in the unit cell, labeled by the number of the tin (yellow Sn–H, and black Sn–Sn distances).

As in the 0 GPa case, there are four different types of tin locations. Their coordination environments are analyzed by a histogram of Sn–H and Sn–Sn distances in Figure 7b. The windows of the histograms at this pressure are from 1.4 to 2.8 Å, smaller than those at 1 atm, shown above in Figure 4b.

Note that the nearest neighbors for a tin atom are now hydrogen atoms (of hydrogen molecules) at ~ 1.9 Å, and the nearest tin atom is at ~ 3 Å. The overall compression is apparent ($V/V_0 = 0.32$), and is by far greater in the H_2 layer, as expected. There must be some interaction between Sn layers and H_2 molecules or between H_2 s, for the H–H bond stretches a little (0.79 Å). The shortest “nonbonded” H–H \cdots H–H approaches are 1.72 Å. For calibration, in the 50 GPa structure of elemental H_2 ($P6_3/m$ space group^[19]), these distances are 1.7–2.0 Å.

It is clear that in this structure the “van der Waals space” between H_2 molecules is now “squeezed out”^[32] while the Sn layers are less affected.

The lowest enthalpy 50 GPa structure we calculate is still unstable when compared to separation into its elements at the same pressure, by +0.61 eV per SnH_4 . It is, however, more stable than the best structures derived by optimizing structures based on other studies of EH_4 molecules where E = Si, Ge and Sn (the red curve in Figure 1; details of the structures will be given elsewhere^[20]), by 0.66 eV per SnH_4 . Once again the enthalpy of the layered structure lies in between the elements and structures that are not layered. If the slabs were thicker, a still more segregated structure is likely to be stabilized.

We thought it possible to go further, and analyze the energetics of the layered structures by decomposing them into their elemental layers, as we did for the $P = 1$ atm structure. This approach proves problematic as it runs into fundamental difficulties of defining appropriate thermodynamic functions and conditions for separate layers as pressure is applied. In particular, it is not possible to apply pressure to a sublattice, at least with the programs available to us, for the sublattice will expand into the vacuum surrounding it.

8. Electronic Structure of the Layered 50 GPa System

At 0 GPa the metallic character of layered structure derives from the tin slabs alone. Given what we have found in the 50 GPa structure (the relatively short Sn–H distances), we expect this phase to be metallic, but with both elements contributing to the DOS at the Fermi level. Figure 8 shows the DOS at $P = 50$ GPa. Note the expected increase in overall band dispersion at 50 GPa relatively to $P = 0$ GPa. The contributions to the DOS, analyzed in the SI, confirm both H and Sn through out the DOS. Note the free-electron-like nature of DOS.

9. A SnH_4 Structure at 140 GPa ($V/V_0 = 0.21$)

The most stable system calculated by us at 140 GPa (Figure 9a) no longer shows elemental slabs (but see below), even though the starting point for geometry optimization was layered. As we show, hydrogens surround the tin atoms, and the closest distances between hydrogens actually increase (relative to

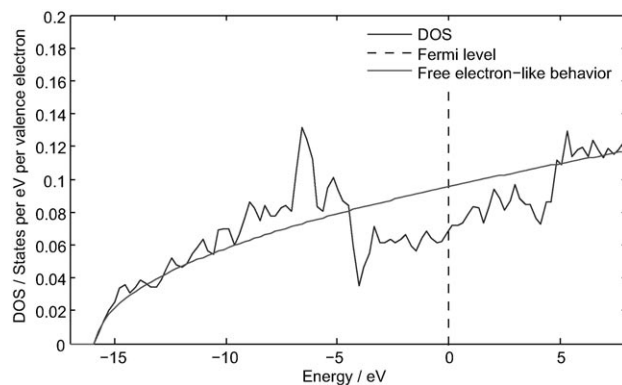


Figure 8. Density of states plot for SnH_4 at 50 GPa, with a superimposed free electron curve to $r_s = 1.829$.

their lower pressure separations). Let us look at the coordination of the H's first.

Figure 9b shows the histogram of H–H separations in the 140 GPa structure. Note that there are no H–H contacts close to the molecular distance of 0.74 Å (or that in elemental H_2 at this pressure, which has H–H bonds of 0.74 Å, and next-nearest H is at 1.3 Å). There are four symmetry-distinct hydrogens in the optimal structure. From the histogram we see that one hydrogen atom (H4) is essentially isolated. That hydride is surrounded by four Sn atoms in a tetrahedron, as shown in Figure 9c, but its closest neighbor is actually another hydrogen atom at 1.78 Å.

Hydrogens 1–3 form interesting helices, with separations (all indicative of partial bonding) indicated in Figure 9d. The nearest interhelix separation is at 2.1 Å. The singling out of a helix is thus somewhat arbitrary (including H–H 1.58, excluding 2.1 Å, as examination of the histogram shows); we really have the beginning of a three-dimensional hydrogen network. Alternatively one could focus on just the shorter H–H contacts (0.98, 1.12 Å) in which case we would say the structure contains H_3 units.

We now turn to the Sn–H separations, Figure 10. There are two distinct Sn atoms in the structure and a histogram of the Sn–H distances is given in Figure 10b. It is not easy to define a Sn coordination environment. The closest Sn–H contact is 1.8 Å, but there are many hydrogens not much further away. If one used the large separation gap at 2.3–2.6 Å for both tins as a cut-off for defining coordination, one would have to call the Sn atoms 15-coordinate. Even though this coordination number seems too high, the general phenomenon of increasing coordination with pressure^[31] makes sense. In Figure 10a,c we use an arbitrary Sn–H cut-off of 2.0 Å, which results in much distorted nonahedra for the two symmetry-distinct (yet almost mirror-image) Sn atoms.

At 140 GPa the electronic structure of the geometry we calculated is not only metallic, but the TDOS shows a characteristic free-electron-like shape (Figure 11). Both Sn and H states contribute to the DOS throughout the filled and unfilled states.

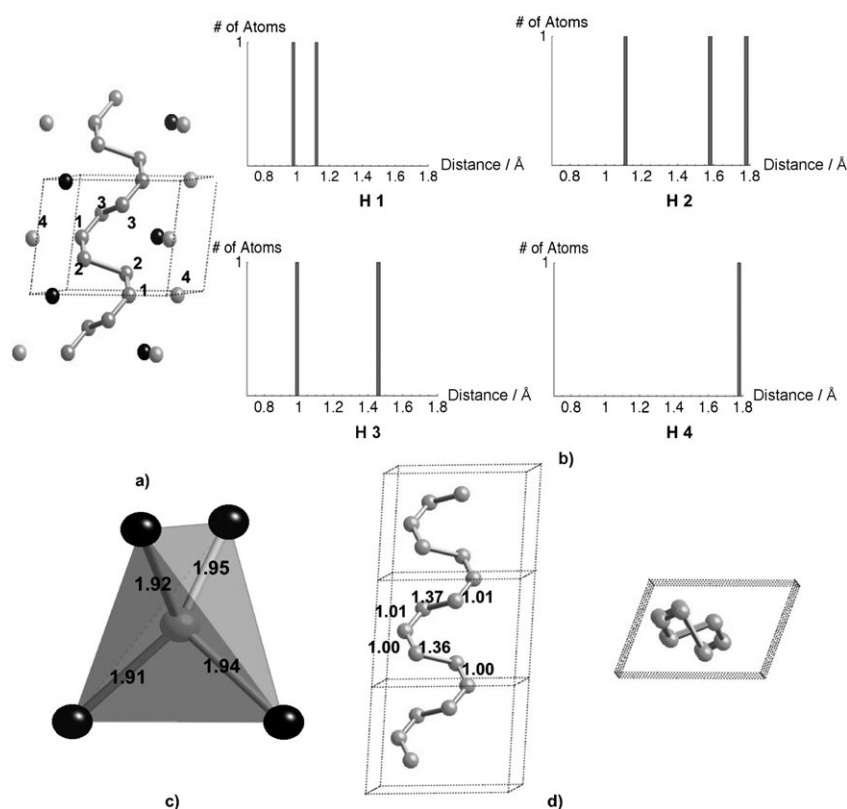


Figure 9. The most stable structure for tin tetrahydride (from our sampling of layered structures at 140 GPa) and its H-H separations. a) Hydrogen atoms are no longer simply paired; some hydrogen atoms form a network—a helix, here we show them in pink. Distinct hydrogens are numbered. b) Histograms of H-H separations by atom type. c) Sn coordination environment of H4. d) Distances in hydrogen helix, and a side view.

10. Energetics of SnH_4 structures at Higher Pressures

The 140 GPa structure is still unstable with respect to the elements. The difference in enthalpy is now reduced, to +0.17 eV per SnH_4 . Could a layered structure (with Z greater than the largest one investigated, $Z=4$) exist at still lower energy than the one we found? We do not know, but it remains a possibility.

Subsequent to our calculations, Gao et al.^[22] reported two lower enthalpy candidates for SnH_4 structures at high pressures, of $Ama2$ and $P6_3/mmc$ symmetry. We calculated these structures over the range of pressures 80–230 GPa. The results are shown in the Figure 12.

Our structural search at $P=140$ GPa was clearly inferior to that of Gao et al.,^[22] who found $Ama2$ and $P6_3/mmc$ structures that are actually more stable than the elements at this pressure. Nevertheless, we feel the “helical” geometry is sufficiently interesting to report here, even if it is not the most stable structure at 140 GPa.

11. When is a Structure Layered?

We return to the question of whether this structure can be considered layered or not. In another view of the 140 GPa

SnH_4 structure, in Figure 13, layers of Sn and H atoms can be seen. The perception of lowered dimensionality in a three-dimensional structure is much in the eye of the beholder. So layers easily float into view in classical structures such as diamond, β -Sn and bcc, yet these are hardly two-dimensional arrays. The perceived layers are just a symptom of a human addiction to pattern recognition. One has to look at the distribution of distances—only when the separations along one axis (perpendicular to the putative layer) are significantly longer than those within a layer could one realistically call the material layered.

The preceding discussion—showing both short Sn–H distances, and the presence of H–H bonded networks—argues, we think, for a three-dimensional nature of the calculated structure.

12. Conclusions

When a tetrahydride is thermodynamically unstable with respect to the elements, as is the case for SnH_4 , the necessary preconditions are present for segregation—in fact, as we propose, to a layering of element slabs. We investigated such layering in SnH_4 , ensuring that the choice of structures allowed H–H bond formation to occur if energetically permitted.

Our optimum structures at 0 and 50 GPa ($r_s=2.67$ and 1.829) show slabs of Sn and molecular H_2 . With increasing pressure, the van der Waals space is squeezed out, as noticed, and Sn–H and H_2 – H_2 separations decrease. At 140 GPa, with $r_s=1.635$ (and we expect the same for greater pressures). Our optimum structures no longer show slabs or the presence of molecular hydrogen. Interestingly, at 140 GPa, the hydrogen atoms are arranged in H_3 units that form helices. Hydridic isolated atoms also occur. As expected, the coordination of tin and hydrogen increases with pressure. However, still more stable structures than those found here (also with H_2 molecular units) have been reported.^[22]

One can analyze the contributions to the enthalpy of slab formation: It takes a good bit of energy to cut the metal layer out of its three-dimensional lattice, less so for the dispersion-force-bound H_2 layer. Bringing the preformed layers together is a stabilizing process, due to what effectively is chemisorption at an interface.

The SnH_4 case may be extreme in that the heat of formation of the molecules is so positive, creating a large thermodynamic

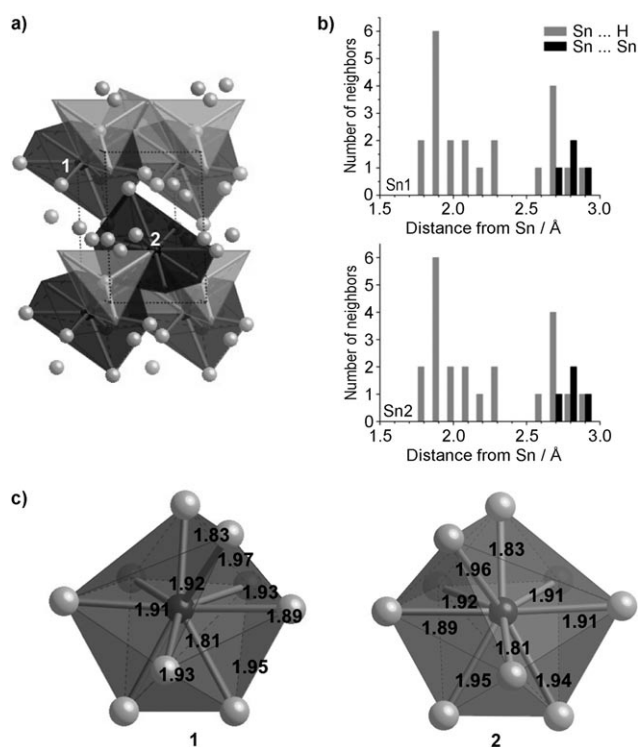


Figure 10. The most stable structure for SnH_4 , from our sampling of layered structures at 140 GPa, and its tin coordination. Slabs are no longer a feature in this structure. a) The unit cell of the optimized system, extended in this view beyond the unit cell (-----). There are two different types of tin locations per unit cell (numbered); b) Portions of distance histograms for the different tin atoms in the unit cell (yellow Sn–H, and black Sn–Sn distances). c) Coordination polyhedra for the two tin atoms; notice that the two tin atoms coordination environments are almost mirror images.

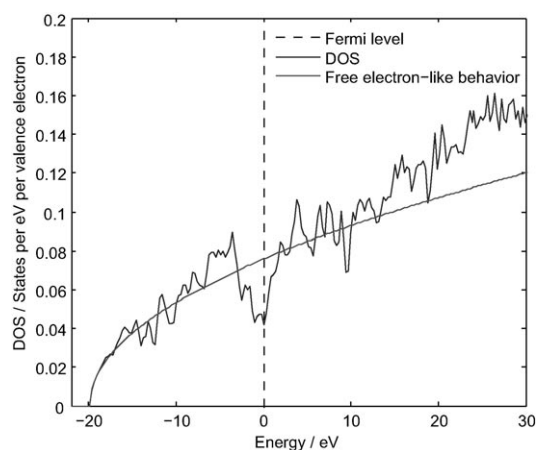


Figure 11. Density of states plot for SnH_4 at 140 GPa, and $r_s = 1.635$.

driving force for segregation and layering. But the lesson of our modeling exercise is clear and likely to be valid generally: *Over a wide range of pressures any compound that has a substantial positive enthalpy of formation is likely to segregate to the elements, and is also likely to form layers or slabs en route to its eventual configuration, which may well include arrangements with more favorable surface to volume energies.*

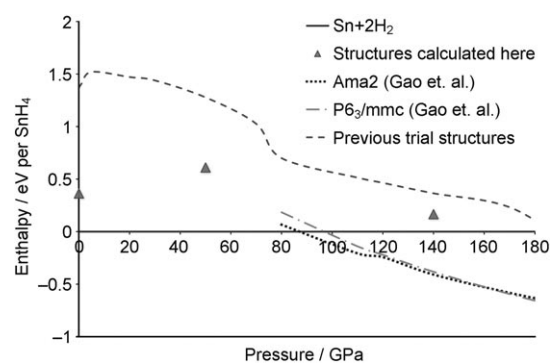


Figure 12. Computed relative stabilities of the structures calculated herein, and *Ama2* and *P6₃/mmc* structures, reported by Gao et al.^[22]

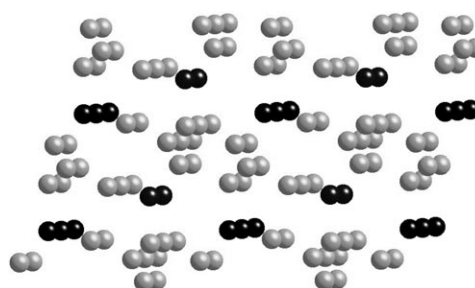


Figure 13. The geometry of the SnH_4 structure calculated by us at 140 GPa, $r_s = 1.635$. It is identical to that shown in Figure 9, but now presented in a view that emphasizes the structure's "layered" nature.

Obviously this does not preclude the possibility (in fact, likelihood) of eventual remixing. Nor does it preclude further rearrangement that may favor the balance of volume and surface free energies, especially at low pressures. As the pressure increases, the situation changes, even when there is a driving force for layering. Unsegregated structures with new bonding patterns may be stabilized and this is where the effect of high pressure becomes truly interesting. In the case of the hydrides, the zero-point energies may yet play a role.

Acknowledgements

Calculations for this work were performed on the Intel Cluster at the Cornell Nanoscale Facility, part of the National Nanotechnology Infrastructure Network (NNIN) funded by the National Science Foundation. We thank Stephen Lee for encouragement. Ji Feng, Xiaodong Wen and Vanessa Labet are acknowledged for helpful discussions. Our work was supported by the National Science Foundation through research grants CHE-091063 and DMR-0904505.

Keywords: bond energy · density functional calculations · high-pressure chemistry · solid-state structures · stannanes

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Received: April 24, 2010

Published online on August 18, 2010