Solid-State Chemistry – Where Chemistry Meets Physics and Materials Science

Richard Dronskowski

Classical Thermochemistry from Quantum Mechanics
Phonons, Excitations, Free Energies, Accuracies
Thermochemical State Functions of High-$T_c$ Superconductors
Predicting Pernitrides, Yet to be Made
Carbodiimides, their Prediction and Synthesis
(A little) Physics of Transition-Metal Carbodiimides
Guanidine and Guanidinates (very fresh)
Summary
Thermochemistry
The Godfather: Josiah Willard Gibbs

V. ON THE EQUILIBRIUM OF HETEROGENEOUS SUBSTANCES.
BY J. WILLARD GIBBS.

"Die Energie der Welt ist konstant, 
Die Entropie der Welt strebt einem Maximum an."

CLAUSIUS.*

The comprehension of the laws which govern any material system is greatly facilitated by considering the energy and entropy of the system in the various states of which it is capable. As the difference of the values of the energy for any two states represents the combined amount of work and heat received or yielded by the system when it is brought from one state to the other, and the difference of entropy is the limit of all the possible values of the integral \(\int \frac{dQ}{l}\),

\(dQ\) denoting the element of the heat received from external sources, and \(l\) the temperature of the part of the system receiving it, the varying values of the energy and entropy characterize in all that is essential the effects producible by the system in passing from one state to another. For by mechanical and thermodynamic contrivances, supposed theoretically perfect, any supply of work and heat may be transformed into any other which does not differ from it either in the amount of work and heat taken together or in the value of the integral \(\int \frac{dQ}{l}\). But it is not only in respect to the external relations of a system that its energy and entropy are of predominant importance. As in the case of simply mechanical systems, (such as are discussed in theoretical mechanics,) which are capable of only one kind of action upon external systems, viz., the performance of mechanical work, the function which expresses the capability of the system for this kind of action also plays the leading part in the theory of equilibrium, the condition of equilibrium being that the variation of this function shall vanish, so in a thermodynamic system, (such as all material systems actually are,) which is capable of two different kinds of action upon external systems, the two functions which express the twofold capabilities of the system afford an almost equally simple criterion of equilibrium.

Classical Computerized Thermochemistry

“G minimizers” for calculating phase diagrams and equilibria based on Gibbs energy data, e.g., SGTE: http://www.sgte.org

data bases:
- experimental, if (!!!) they do exist
- theoretical calculations based on
  a) electronic energies ($T = 0 \text{ K}$) and
  b) temperature-dependent contributions
From Molecules & Solids to the Gibbs Energy

\[ G(p, T) \]

\[ \mathcal{H}\Psi = E\Psi \]

Stationary (i.e., time-independent because the property clearly does not depend on \( t \)) Schrödinger equation needs to be solved without any empirical parameters.
The Hamilton Operator, $N$ electrons & $M$ nuclei

\[ \mathcal{H} = - \sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{A=1}^{M} \frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{1}{4\pi\varepsilon_0} \left( \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A e^2}{r_{iA}} - \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^2}{r_{ij}} - \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B e^2}{R_{AB}} \right) \]

simplifies (just a little) to give

\[ \mathcal{H} = - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \]
Density-functional theory: averaged potential

\[ \nu_{\text{eff}}(\mathbf{r}) = \nu(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \nu_{\text{XC}}(\mathbf{r}) \]

\[ \nu_{\text{XC}}(\mathbf{r}) = \frac{\partial E_{\text{XC}}\{\rho(\mathbf{r})\}}{\partial \rho(\mathbf{r})} \]

electron-electron interactions (\textit{eX}change and \textit{C}orrelation) become parameterized – without \textbf{adjustable} parameters – to arrive at an effective one-electron \textbf{Kohn–Sham} theory; local-density approximation (LDA) and generalized-gradient approximation (GGA) … plus many others!
$T = 0$ K: Electronic Energy of the Ground State

solid-state materials: very often density-functional theory

Born–Oppenheimer approximation: nuclei are fixed, electrons just move in the nuclear potential

$\rightarrow$ purely electronic energies

no temperature-dependent contributions whatsoever
Tin pest

the two tin allotropes (or elemental polymorphs):

\[ \alpha\text{-Sn} \ (\rho = 5.8 \text{ g cm}^{-3}, \ T < 13 \ ^\circ \text{C}) \]
\[ \beta\text{-Sn} \ (\rho = 7.3 \text{ g cm}^{-3}, \ T > 13 \ ^\circ \text{C}) \]

their phase transition is dubbed *tin pest* and may be induced either by *pressure* or *temperature*
Electronic Ground State Energy: Calculus

\[ E_0 (V) \approx U (0 \text{ K, } V) \]

\[ H (p, 0 \text{ K}) \approx E_0 (V) + pV \]

\[ p = -\frac{dE_0 (V)}{dV} \]

\[ E(V) = E(V_0) + B_0 \frac{V}{B'_0} \left[ \frac{(V/V_0)^{B'_0}}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \]

*empirical equation of state*
Tin pest: enthalpy against pressure by DFT

\[ \Delta H / \text{kJ mol}^{-1} \]

\[ \rho / \text{GPa} \]

\[ \beta - \text{Sn} \]

\[ \alpha - \text{Sn} \]
Pressure Experiment: How large is 1 Gigapascal?

\[ p = \frac{F}{A} = \frac{m \ a}{A} \]

with

\[ m = 60 \text{ kg}, \ a = 9.81 \text{ m s}^{-2} \]

and \[ A = 1 \text{ cm}^2 \]

yields 5.9 MPa only!

→ reduce area or increase mass (both a bit difficult)
Temperature: Cu heat capacity

![Graph showing temperature versus heat capacity for different models and comparisons with experiments.](graph.png)
Temperature-dependent Energy Contributions

- *harmonic* vibrational free energy $\rightarrow A_{\text{ph}} (A_{\text{vib, harm}})$
- $T$-dependent *electronic excitations* $\rightarrow A_{\text{el}}$
- *configurational entropy* contribution $\rightarrow A_{\text{conf}}$
- *magnetic* contribution $\rightarrow A_{\text{mag}}$
- *anharmonic* vibrational contributions $\rightarrow A_{\text{vib, anhar}}$

Helmholtz energy $A$ is a sum:

$$A = E_0 + A_{\text{ph}} + A_{\text{el}} + A_{\text{conf}} + A_{\text{mag}} + A_{\text{vib, anhar}} + \ldots$$

insulators, semiconductors: $A \approx E_0 + A_{\text{ph}}$
Phonon band structure of 1dim H chain...
... and of face-centered cubic copper

\[ k = \frac{2\pi}{a} (1,0,0), \lambda = a \]
Copper at the X point: transversal phonon
... and of face-centered cubic copper

X point: \( k = \frac{2\pi}{a} (1,0,0) \), \( \lambda = a \)
Copper at the X point: longitudinal phonon
Quasi-harmonic approximation for copper

\[ A(V, T) = E(V, T = 0 \text{ K}) + A_{\text{ph}}(V, T) \{ + A_{\text{el}}(V, T) \} \]
Anharmonicity proof: copper lattice expansion
Gibbs Energy $G$ from Helmholtz Energy $A$ (BaO)

\[ G = A + pV = A - \frac{dA}{dV} \cdot V \]
Hellmann\(^1\)–Feynman\(^2\) Forces (\(^1\)1933 and \(^2\)1939)

\[ F = -\frac{dE}{dR} = -\left\langle \Psi \left| \frac{\partial \mathcal{H}}{\partial R} \right| \Psi \right\rangle \]

Provided a high-quality wave function, the force is equivalent to the Coulomb force of a given nucleus on the other nucleus and the electronic charge cloud. Unfortunately, small errors in the calculation of the latter translate into large errors for the forces.

Hans Hellmann

Richard Feynman
Also by Hans Hellmann: Pseudopotentials

\[ \psi(k,r) \]

one-dimensional Na-3s Bloch function at \( X \)

the world’s first pseudopotentials: Na and Cs

\[ V_{\text{pseudo}}(r) = -(1 - Ae^{-2\kappa r})/r \]

\[ V(r) = -1/r \]

\( r \) (Bohr)

→ plane waves, thus reliable forces!
Vibrational Frequencies \textit{ab initio}

Various methods exist:

a) molecular dynamics (accurate but slow)

b) \textit{frozen phonon}: “snapshots” of vibrational modes

c) perturbation theory (\textit{linear response})

d) \textit{ab initio} force-constant (“\textit{direct}”) method:
forces derived from displacements of single
atoms in supercells \((a, b, c > 10 \text{ Å})\) using the proper
codes: FROPHO\textsuperscript{1}, PHONOPY\textsuperscript{2}, PHONON\textsuperscript{3} etc.)

1: http://fropho.sourceforge.net/
2: http://phonopy.sourceforge.net/
3: http://wolf.ifj.edu.pl/phonon/
Heat capacity $C_p$

The temperature dependence of the Gibbs Energy $G$ is entirely determined by $C_p$

$$G = H - T \, S$$

$$H = H^\text{ref} + \int_{T_\text{ref}}^T C_p \, dT$$

$$S = S^\text{ref} + \int_{T_\text{ref}}^T \frac{C_p}{T} \, dT$$

$H^\text{ref} \equiv \Delta H_f (298 \, \text{K})$

$S^\text{ref} \equiv S (298 \, \text{K})$
Electronic Excitations

\[ A_{el}(V,T) = E_0(V) + \Delta A_{el}(V,T) \]

\( T \)-dependent occupancy of the bands (Fermi–Dirac statistics)

fairly unimportant for nonmetallic systems

Metals: electronic-excitation part of \( C_V \) about 100,000 times smaller than phononic part
Gibbs energy

\[ G(p, T) = A(V, T) + pV \]

Additional contributions

\[ A_{\text{conf}}(T), A_{\text{mag}}(V, T), A_{\text{vib, anharmonicity}}(V, T), \ldots \]

Helmholtz energy

\[ A(V, T) = A_{\text{el}}(V, T) + A_{\text{ph}}(V, T) + \ldots \]

Electronic excitation

\[ A_{\text{el}}(V, T) = E_0(V) + \Delta A_{\text{el}}(V, T) \]

Vibrational excitation

\[ A_{\text{ph}}(V, T) \]

Force

\[ F = -\frac{dE}{dr} \]

Energy

\[ E_0(V) \]

Structure

\[ H \Psi = E \Psi \]
Tin pest: Gibbs energy against **temperature**

\[ \Delta G / \text{kJ mol}^{-1} \]

Error in \( T \) ca. 90 K, in \( G \) ca. 0.8 kJ mol\(^{-1} \)
Superconductors & Pernitrides
High-temperature superconductors

\( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) buffer (MgO, ZrO\(_2\)...) nickel alloys
Y-123-6.5: $T$-dependent phases \textit{ab initio}
Y-123-6.5: Gibbs formation energy

\[ \Delta G_R / \text{kJ mol}^{-1} \]

\[ T / \text{K} \]

Thermochemical Wire Model of Y–Ba–Cu–O

self-consistent thermochemical data set based on 24 phases (11 metallic ones, 12 oxidic matter plus the melt)

unpublished, on purpose
High-Temperature Superconducting Induction Heater

More than 80% of the total energy contribute to the heating of the billet
Principles of Induction Heating

conventional

superconducting

Control Losses

Coil Losses

Billet

Control Losses

Drive Losses

Coil Losses

Billet
Metal pernitrides (existing and predicted)

- **BaN₂**
- **PtN₂**
- **OsN₂**
- **IrN₂**
- **BeN₂**
- **MgN₂**
- **CaN₂**
Platinum “Nitride”: the Obvious Discrepancy

Le Chatelier’s principle violated

product phase is less dense than the elements!
Platinum “Nitride”: Enthalpy = \( f(\text{Pressure}) \)

![Graph showing \( \Delta H \) vs. \( \rho \) for different substances: [CaF\(_2\)], [NaCl], [PtS], [ZnS], and [FeS\(_2\)]. Elements are indicated on the graph. The source is J. von Appen, R. Dronskowski, Angew. Chem. Int. Ed. 2006, 45, 4365.]
Barium & Platinum Pernitride: N–N Bond
Prediction of FeN₂

rhombohedral $\overline{R3m}$

$\Delta H_R = +61 \text{ kJ mol}^{-1} \text{ at } T = 0 \text{ K}$

$B_0 = 192 \text{ GPa}$

$N\text{–N} = 1.275 \text{ Å}$

$\mu = 1.68 \mu_B$ (ferromagnetic)
FeN$_2$ synthesis (prediction) at $T = 1000$ K

upper pressure limit: full finite-temperature calculations for all solids, approximate classical heat-capacity for elemental nitrogen

Carbodiimides
Nomenclature of “NCN” chemistry

\[
\begin{align*}
\text{H}_2\text{N} & \equiv \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{H} \\
\text{carbodiimide,} & \\
\text{matrix curiosity} & \\
\text{H}_2\text{NCN} & \text{cyanamide,} \\
& \text{weak acid}
\end{align*}
\]

\(\text{H}_2\text{NCN}\) is a fundamental, commercially available cheap chemical (CYANAMIDE/DEGUSSA AG), produced on a very large scale everywhere on the planet.
“NCN” chemistry in a nutshell

carbodiimide $\text{NCN}^{2-}$

(not nitride $\text{N}^{3-}$)

is the nitrogen analogue of

oxide $\text{O}^{2-}$

note: $\text{GaN} = \text{Ga}^{3+}\text{N}^{3-}$; $\text{CaO} = \text{Ca}^{2+}\text{O}^{2-}$; thus, there can be no “$\text{CaN}$”
Solid Carbodiimides vs. Cyanamides

N. G. Vannerberg
*Acta Chem. Scand.* **1962**, *16*, 2263

X. Liu, A. Decker, D. Schmitz, R. Dronskowski
**Carbodiimides/Cyanamides in the Periodic Table**

The periodic table of elements with a focus on carbodiimides and cyanamides. The table includes the element symbols, atomic numbers, and other relevant chemical properties. The table is sourced from [http://www.pse-online.de](http://www.pse-online.de).
Computational Stability Trends for “MNCN”

all “MNCN” phases are enthalpically (H) unstable!

all “MNCN” phases are also thermodynamically (G) unstable!

M. Launay, R. Dronskowski, 
M. Launay, R. Dronskowski, 
MnNCN: Synthesis – in 2005!

600 °C: \( \text{MnCl}_2(s) + \text{ZnNCN}(s) = \text{ZnCl}_2(g) + \text{MnNCN} \)

[CaNCN] type

CuNCN with first-order Jahn–Teller effect

made at room temperature in aqueous media

orthorhombic Cmcm

Cu–N = 2.001(2) Å (4×),
2.613(3) Å (2×)

C–N = 1.227(4) Å
N–C–N = 176.4(5)°

X. Liu, M. A. Wankeu, H. Lueken,
CoNCN and NiNCN

made at 400 °C

stretched [NiAs] type,

hexagonal $P6_3/mmc$,

$R_1 = 0.0158/0.1045$

Co–N = 2.168(1) Å (6×)

Ni–N = 2.119(8) Å (6×)

C–N = 1.226(2) Å

N–C–N = 180°

FeNCN: Structure and Magnetic Properties

antiferromagnet,
$T_N = 345 \text{ K}$, $\mu_{\text{eff}} = 3.9$

$P6_3/mmc,$
$a = 3.2689(2),$ 
$c = 9.401(1) \text{ Å},$
Fe–N = 2.201(6) Å

X. Liu, L. Stork, M. Speldrich, H. Lueken,
Transition-metal oxides vs. carbodiimides

MnO   FeO   CoO   NiO   CuO

archetypal 3d transition-metal oxides; competition between electronic Coulomb repulsion and interatomic attraction ("hybridization"); there results metal-insulator (Mott) transitions, colossal magnetoresistance, charge ordering, orbital ordering, spintronics, "orbitronics", superconductivity... three decades (and more) of solid-state physics

MnNCN   FeNCN   CoNCN   NiNCN   CuNCN

a novel, simple class of nitrogen-based 3d transition-metal pseudo-oxides; "hybridization" is chemically changed (N vs. O); all enthalpically unstable; much more difficult to make than oxides
MnO: Magnetic structure from the 1950s

MnNCN: neutron scattering at SV7

complicated temperature-dependent behavior mirrors the magnetic susceptibility data
continuous set of different magnetic orderings
statistics insufficient for structure solution
MnNCN: pure magnetic scattering at DNS
MnNCN: Spin Orientations within $ab$ Plane

Chromium(III) Carbodiimide

metathesis at 550 °C: \( \text{Cr}_2(\text{NCN})_3 \)

\( R\bar{3}c; \ a = 5.4751(1) \ \text{Å}, \ c = 27.9696(3) \ \text{Å}, \)

\( \text{Cr–N} = 2.081(5) \ \text{Å} \ (3\times), \ 2.101(4) \ \text{Å} \ (3 \times), \)

\( \text{C–N} = 1.208(4) \ \text{Å}, \ \text{N–C–N} = 178.0(7)° \)
Cr$_2$(NCN)$_3$ is a **ferromagnetic** material

CONDON analysis:
\[ \lambda_{mf} = 8.589 \times 10^7 \text{ mol cm}^{-3}, \text{ GOOF} = 1.3\% \]
\[ \theta = 178 \text{ K}, ^4A_2 \text{ ground state} \]
paramagnetic moment: 3.6 $\mu_B$

**larger** magnetization than $\gamma$-Fe$_2$O$_3$
\textbf{Cr}_2(\text{NCN})_3: \textit{Correlated Electronic Structure}

\begin{equation*}
\begin{aligned}
+ + + + \quad \text{(FM),} \\
+ - + - \quad \text{(AFM1, Cr}_2\text{O}_3) , \\
+ + - - \quad \text{(AFM2, \text{\(\alpha\)}-Fe}_2\text{O}_3) , \\
+ - - + \quad \text{(AFM3)} \rightarrow \text{FM is lowest in GGA}+U \ (U = 4.0 \text{ eV})
\end{aligned}
\end{equation*}

mixed charge-transfer/Mott–Hubbard ferromagnetic insulator/semiconductor with ca. 1.7 eV band gap

X. Tang, H. Xiang, X. Liu, M. Speldrich, R. Dronskowski, 
\textit{Angew. Chem. Int. Ed.} \textbf{2010}, \textit{49}, 4738
CuNCN, the nitrogen analogue of CuO

CuNCN is a many-body “spin-liquid” phase

zero magnetic scattering from polarized neutrons

no magnetic ordering from $\mu$SR, ESR, NMR and magnetic susceptibility

Guanidinates
Guanidine and other important biomolecules

Guanine

Creatinine

Guanidinum
Carbonic Acid, Urea, Guanidine

Synthesis: 1991  1828  1861

Crystal Structure: (?)  1923 (Weissenberg)  2009
Guanidine: Crystal structure and packing

Guanidine: DFT hydrogen positions & bridges

V. L. Deringer, V. Hoepfner, R. Dronskowski,
*J. Phys. Chem. C*, submitted
Why Guanidine-based Solid-State Chemistry?

$\text{NCN}^{2-}$ matches $\text{O}^{2-}$, therefore

MnNCN  FeNCN  CoNCN  NiNCN  CuNCN

$\text{C(NH)_3}^{2-}$ matches $\text{CO}_3^{2-}$
Guanidinate, Guanidine, Guanidinium

\[
\begin{align*}
\text{CN}_3\text{H}_4^- & \quad \cdots \text{CN}_3\text{H}_3^{2-}, \text{CN}_3\text{H}_2^{3-}, \text{CN}_3\text{H}_4^{4-}, \text{CN}_3^{5-}
\end{align*}
\]
“Guanidine […] shows not the slightest acid properties in water solution. On the contrary, it behaves as a strong base.”

“Potassium amide in excess added to a solution of guanidine nitrate results in the formation of dipotassium guanidine which is insoluble.”

“Monosilver guanidine was obtained by the action of guanidine nitrate on silver amide. The salt is insoluble in liquid ammonia. It was not obtained in crystalline form.”
Novel Solid-Solid Route

$$\text{CN}_3\text{H}_5(\text{s}) + \text{RbH}(\text{s}) \rightarrow \text{RbCN}_3\text{H}_4(\text{s}) + \text{H}_2(\text{g})$$
Crystal Structure

*Pnma, Z = 4*

\[ a = 6.9369(4) \text{ Å} \]
\[ b = 7.0009(3) \text{ Å} \]
\[ c = 7.5087(4) \text{ Å} \]

\[ R_p = 0.054 \]
\[ R_{\text{Bragg}} = 0.037 \]
Guanidinate itself

\[
\begin{align*}
\text{HN} & \quad 1.336 \text{ Å} \\
\text{NH} & \quad 1.437 \text{ Å} \\
\text{NH}_2 & \\
\end{align*}
\]

\textit{GAUSSIAN 03 MP2(full)6-311+G(d,p)}

Infrared spectra show NH stretching vibrations at 3278 and 3099 cm\(^{-1}\) → H bridging bonds

Summary

Thermochemistry from Schrödinger using *plenty* of CPU time: electronic ground state → forces → phonon frequencies → Helmholtz energy → Gibbs energy

Better G functions for existing superconductors, non-existing high-pressure (pernitride) phases predicted

Carbodiimides = quasi-oxides based on nitrogen atoms, difficult to make → transition-metal carbodiimides yield new physics not seen for the oxide analogues

Guanidinates = quasi-carbonates based on nitrogen, *very* difficult to make; we are currently working on the transition-metal representatives
Happy Theorists & Experimentalists in Nov. 2008
Emperor Karl and the Aachen Cathedral

Karl der Große
747–814 AD