Comparing thermodynamic data for monatomic and diatomic gases from ab-initio and CALPHAD data

JÜLICH
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A report on project done for completion of

Mini Thesis

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Scope & limitations

- How can we use a combination of **ab initio** modelling and **statistical mechanics** use to predict the thermodynamics of (ideal) gases?
- Understand the NIST-JANAF expressions
- Dilute (idea) gas
- No electronic excitations
- No anharmonic vibrational contributions

Journal of
Physical and Chemical Reference Data

Monograph No. 9

NIST-JANAF Thermochemical Tables
Fourth Edition
Part I, Al-Co

Malcolm W. Chase, Jr.

National Institute of Standards and Technology
Gaithersburg, Maryland 20899-0001

Monatomic gas

- Many-body wave function factorises into single particle wave functions for dilute gas (eventually obeying proper Bose/Fermi symmetry)

$$|\psi\rangle = \psi_1\rangle \otimes |\psi_2\rangle \otimes \psi_3\rangle \ldots$$

- Single particle Schrödinger equation (non-interacting)

$$H|\psi_i\rangle = e_i|\psi_i\rangle \Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = e_i\psi(\mathbf{r})$$

- Standing wave solution in box of size L^3

$$\psi_i(\mathbf{r}) \sim \exp(i\mathbf{k}\cdot\mathbf{r}), \quad k_j L = n_j\pi, \quad n_j = 1,2,\ldots$$

Monatomic gas

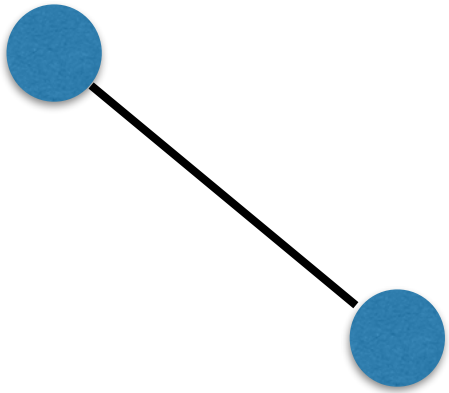
- Discrete energy levels $e_i = \frac{\hbar^2 \pi^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$
- Canonical partition function $Z = \mathrm{tr} \exp(-\beta H)$
- Free energy $F = -kT \ln Z \approx -NkT \ln \frac{V(2\pi mT)^{3/2} e}{h^3 N}$
- Ideal gas law $p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V}$
- Heat capacity $C_V = \frac{3}{2} NkT, \qquad C_p - C_V = Nk$

Diatomic gas

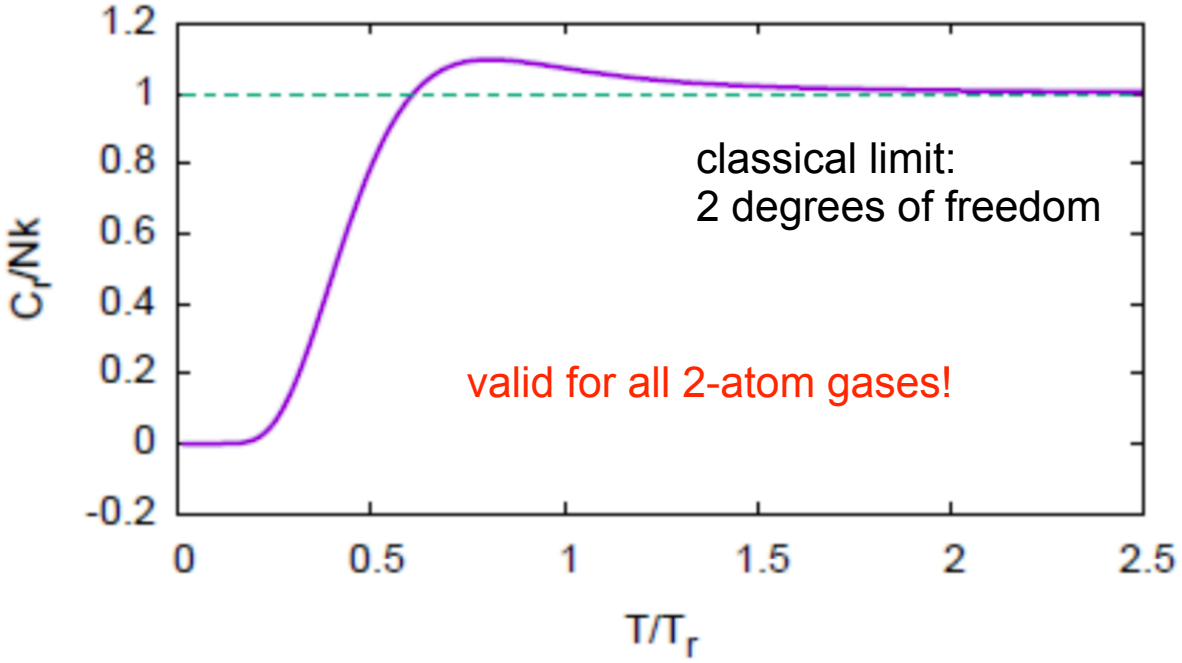
- Interaction between atoms $H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(\mathbf{r}_1 - \mathbf{r}_2)$

- Apart from center of mass motion we have **rotational** and **vibrational** contributions
- Discrete excitations of rigid body rotations

$$e_r = \frac{\hbar^2 \ell(\ell+1)}{2mr_0^2}, \quad \ell = 0,1,2,\ldots$$



Rotational contribution



Rotational temperature

$$T_r = \frac{\hbar^2}{2mr_0^2k}$$

e.g. O_2: $T_r \sim 2K$

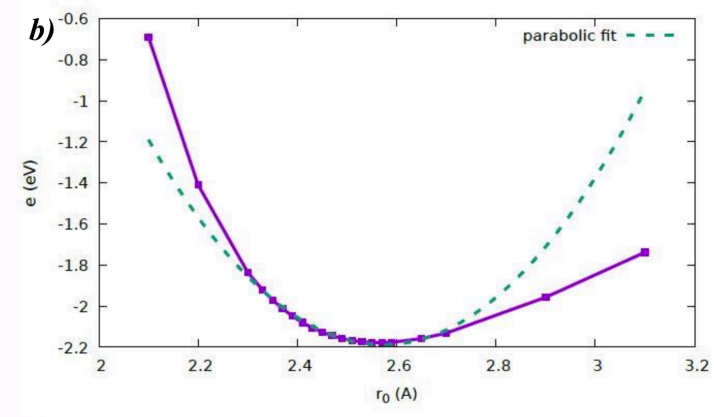
Vibrational contribution

- Harmonic approximation of interaction potential

$$V(r) \approx V_0 + \frac{1}{2} m\omega^2 (r - r_0)^2$$

- Quantum excitations of oscillator

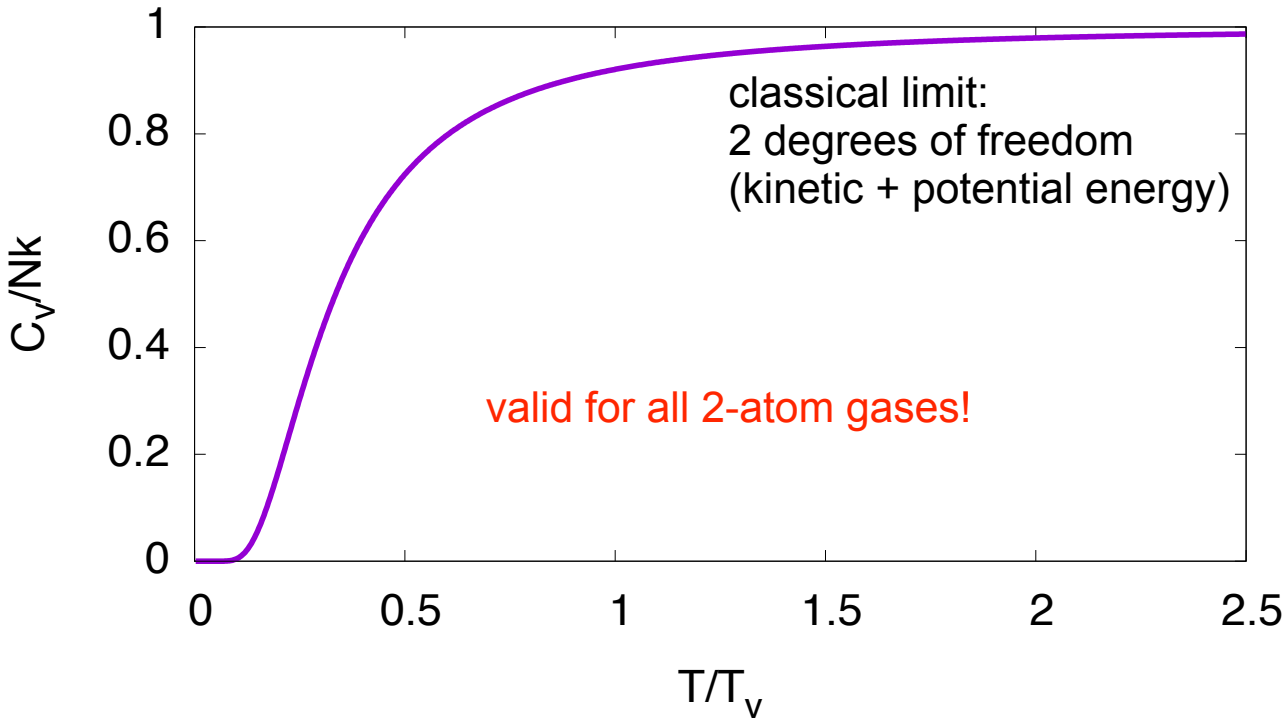
$$e_v = \hbar\omega \left(n + \frac{1}{2} \right), \quad n = 0,1,2,\ldots$$



- Vibrational contribution to heat capacity

$$C_v = Nk \frac{(T_v/T)^2}{4\sinh^2(T_v/2T)} \qquad T_v = \hbar\omega/k$$

Vibrational contribution

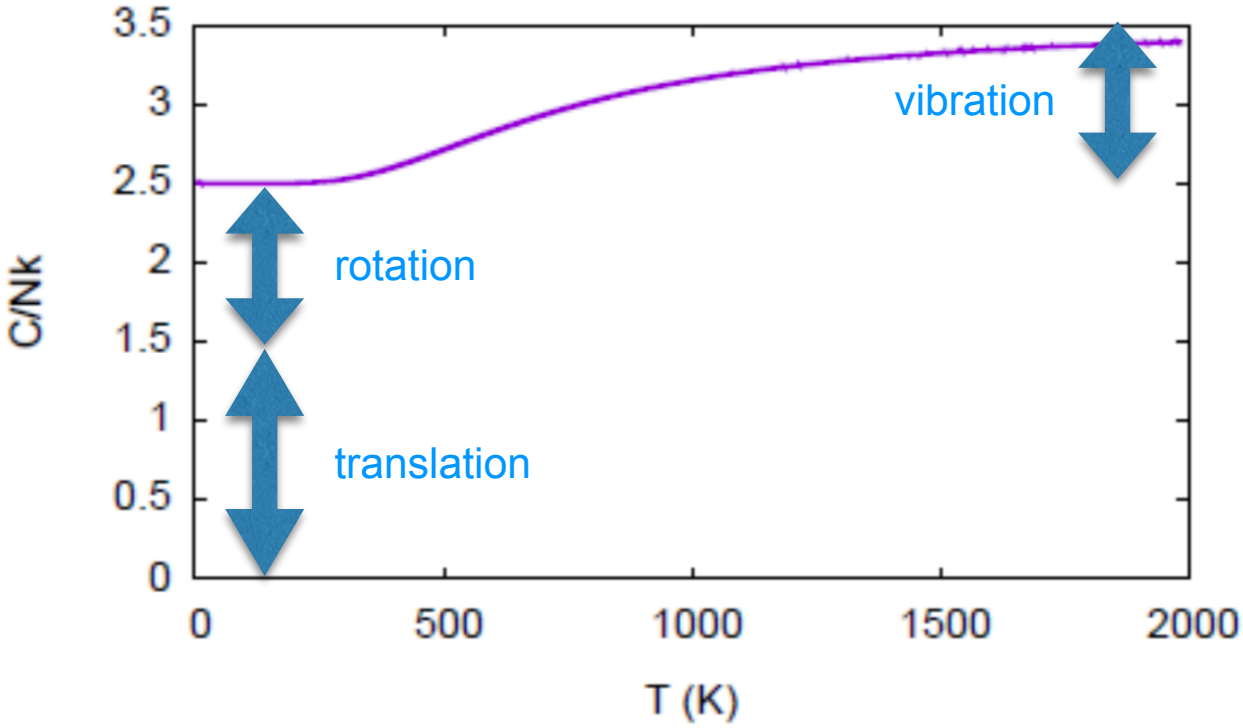


Vibrational temperature

$$T_v = \hbar\omega/k$$

e.g. O_2: $T_v \sim 2300$ K

Heat capacity C_V



Ab initio simulations

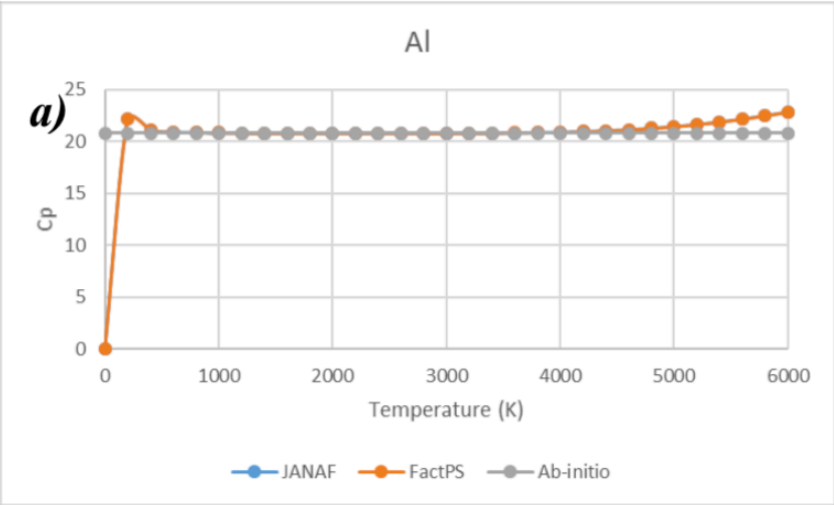
- Extract (parabolic approximation of) interaction potential V(r)
- VASP simulations (PBE; periodic boundary conditions)
  - Place single molecule in large box, calculate energy as function of atomic distance r: Extract equilibrium separation + vibrational frequency
  - Optimize energy cutoff, box size (k point mesh refinement not necessary, gamma point sufficient)
  - Reference configuration: Equilibrium crystal

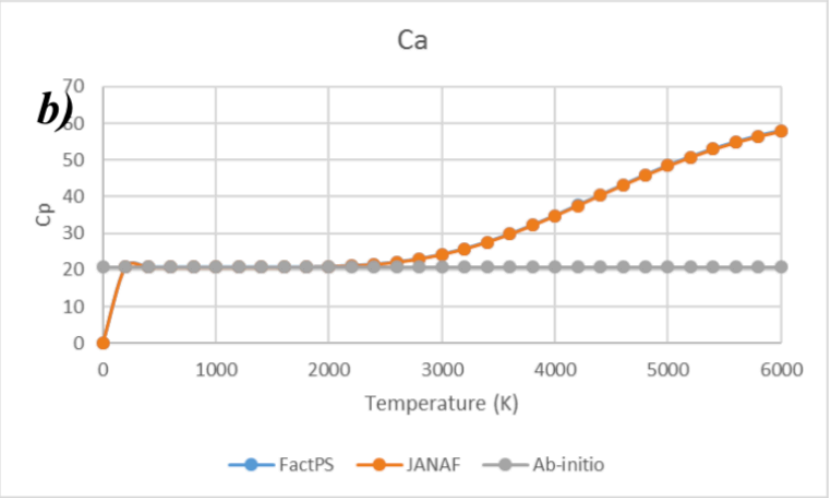
Formation enthalpy

@ room temperature

Monatomic gas						
Elements	E_0 Gas (eV/atom)	E_0 Solids (eV/unit cell)	E_0 Solids (eV/atom)	ΔH_f (kJ/mol)	NIST JANAF ΔH_f (kJ/mol)	Difference (kJ/mol)
Ag	-0.210	-10.824	-2.706	240.866	284.144*	-43.278
Al	-0.229	-14.966	-3.741	338.974	327.300	11.674
Au	-0.181	-12.739	-3.185	289.822	358.285*	-68.463
Ca	-0.041	-7.671	-1.918	181.087	177.300	3.787
Cu	-0.247	-14.898	-3.725	335.545	336.400	-0.855
Pb	-0.614	-14.227	-3.557	283.979	195.880	88.099
Pd	-1.475	-20.751	-5.188	358.261	378.234*	-19.973
Pt	-0.527	-24.228	-6.057	533.613	565.258*	-31.645
Rh	-1.171	-29.093	-7.273	588.870	556.89*	31.980
Sr	-0.085	-6.543	-1.636	149.652	164.400	-14.748

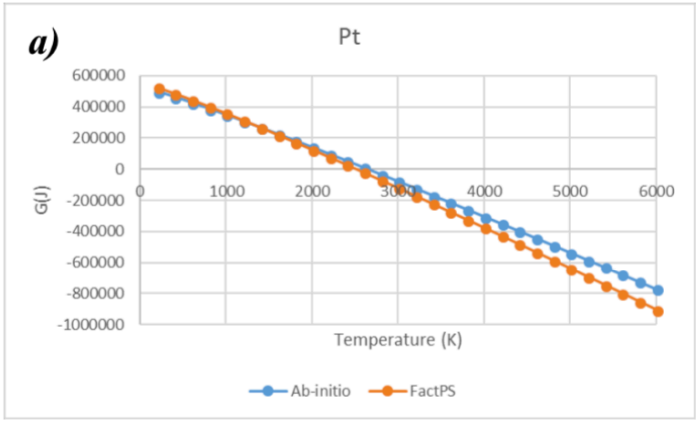
Monatomic gases: Heat capacity

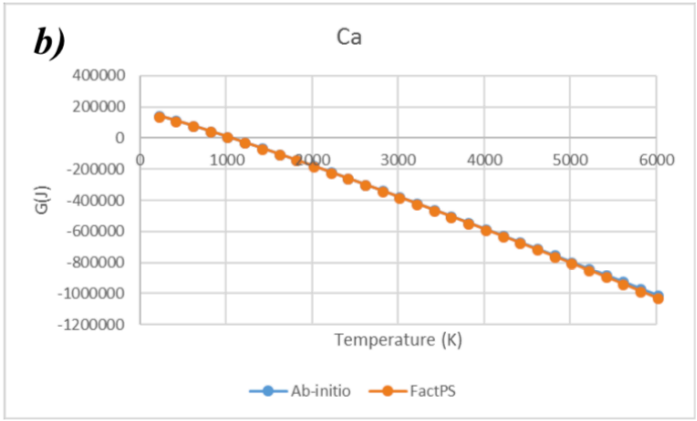


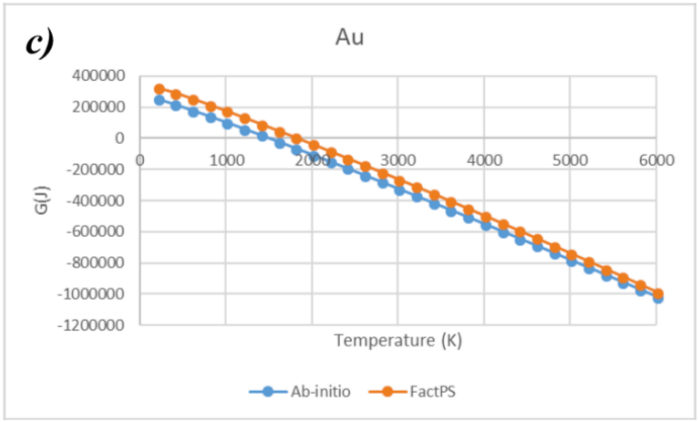


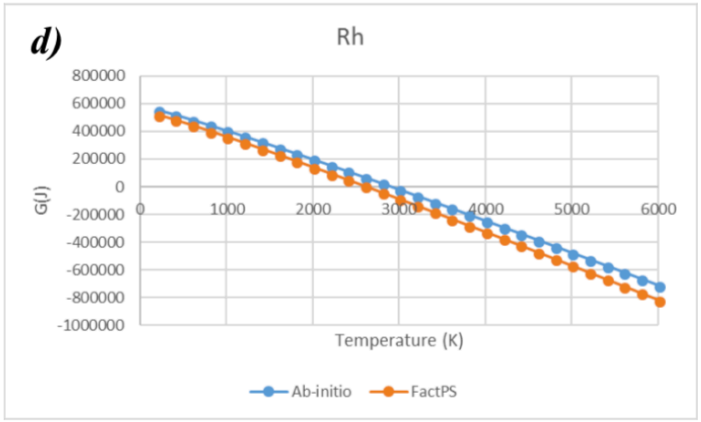
- High temperature deviations due to electronic excitations

Monatomic gas: Gibbs free energy





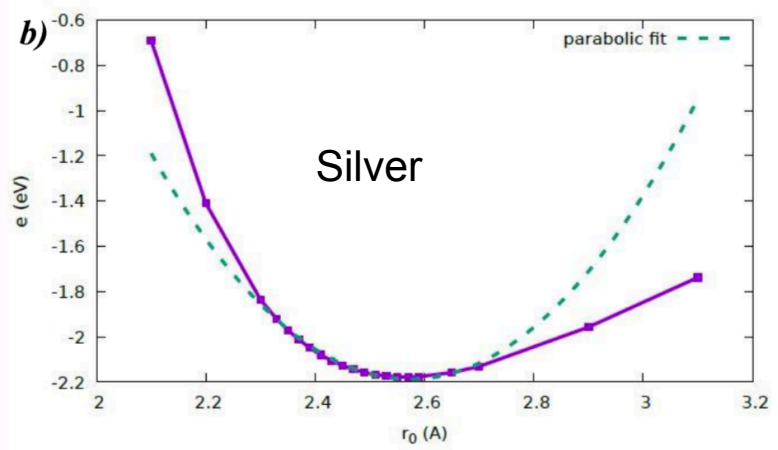


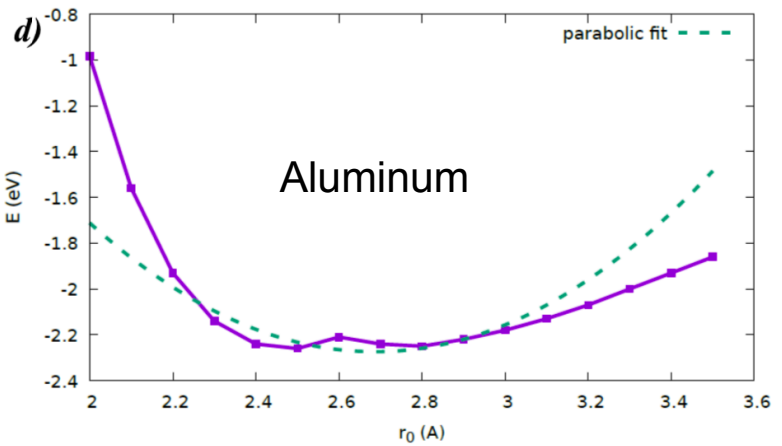


Diatomic gas

Diatomic gas molecule						
Elements	E_0 Gas (eV/molecule)	E_0 Solids (eV/unit cell)	E_0 Solids (eV/molecule)	ΔH_f (kJ/mol)	NIST JANAF ΔH_f (kJ/mol)	Difference (kJ/mol)
Ag	-2.188	-10.824	-5.412	311.090	409.99*	-98.980
Al	-2.274	-14.966	-7.483	502.655	486.300	16.355
Au	-2.703	-12.739	-6.369	353.818		
Ca	-0.012	-7.671	-3.835	368.971	341.920	27.051
Cu	-2.748	-14.898	-7.449	453.621	485.430	-31.809
Pb	-3.725	-14.227	-7.113	326.945	336.400	-9.455
Sr	0.039	-6.543	-3.272	319.447	310*	9.447

* Data taken from FactPS database at 298.15 K





Diatomic gas: Heat capacity

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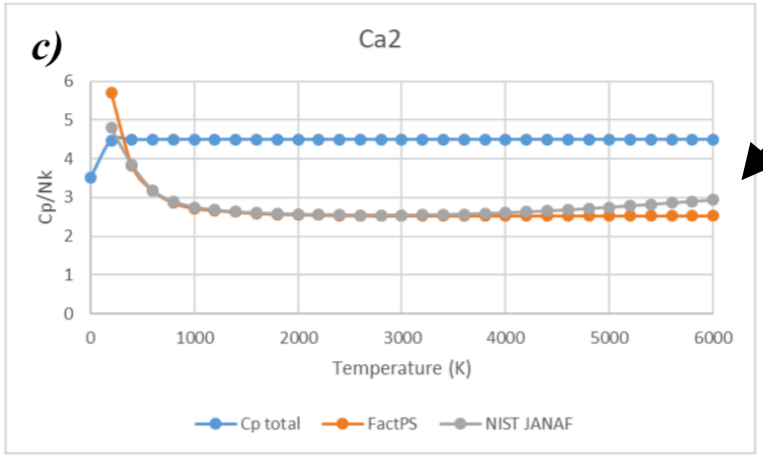
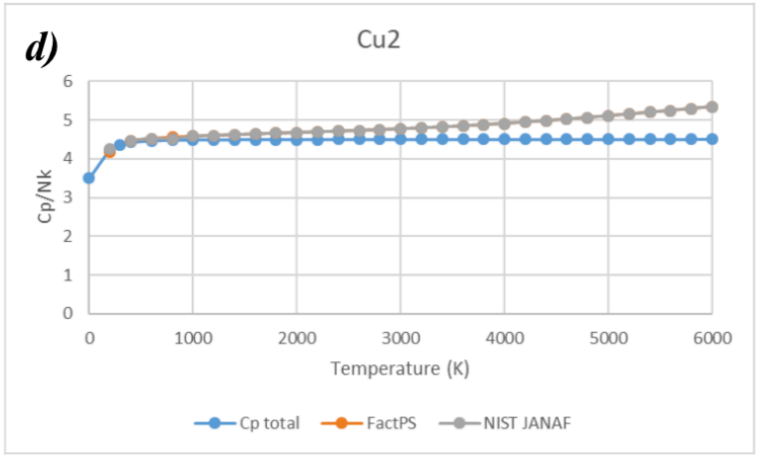
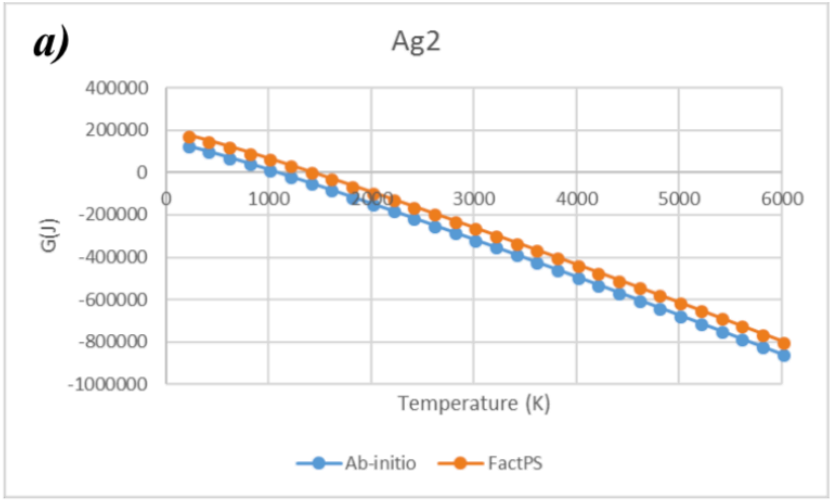
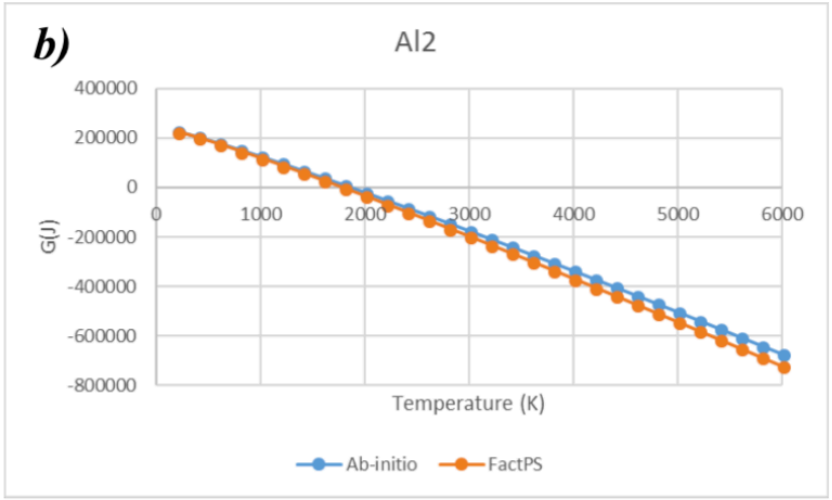




- We don’t have vibrational anharmonicity + electronic excitations

Diatomic gas: Gibbs free energy





Conclusions

- The combination of (standard) statistical mechanics + (simple) ab initio parameter determination can lead to useful (and easy to get) thermodynamic descriptions of ideal gases
- Presently lacking:
  - anharmonicities
  - electronic excitations
  - more complex molecules
  - Higher densities