CHAMELEON: Virtual Laboratories for Exoplanets and Planet-forming Discs
CHAMELEON: Topics & Tools

Virtual Laboratories

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<th>GCMs</th>
<th>STAND</th>
<th>BioDiMo</th>
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<td>Kin. chemistry</td>
<td>Kin. chemistry</td>
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<tr>
<td>heat + cool</td>
<td>eq. chemistry</td>
<td>heat + cool</td>
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<tr>
<td>RT</td>
<td>UV, X-ray</td>
<td>2D hydrostatic disk</td>
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<td>mixing</td>
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<td>predict observables</td>
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<td>RT</td>
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<td>predict observables</td>
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<td>GGCHEM</td>
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<td>MCMAX</td>
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</table>
• **Thorsten Balduin**, start 27/10/2020, St Andrews (→ P. Woitke)

• **secondment**: Copenhagen (→ U. Joergensen)

  → **ESR 6**: Charge conservation and cloud formation in planet atmospheres  → Nanna Bach-Moeller

  → **ESR 8**: The warm chemistry in the inner disk  → Jayatee Kanwar

  → **ESR 13**: Modelling lightning in 3D GCMs and the detection of biosignatures  → Marrick Braam

• **Till Käufer**, start 27/09/2020, St Andrews (→ P. Woitke)

• **secondment**: SRON/Groningen (→ M. Min)

  → **ESR 11**: Machine learning for inferring physical and chemical parameters from exoplanet observations  → Francisco Ardevol

  → **ESR 10**: The disk-planet connection: exoplanet composition informed by disc models  → Areli Castrejon
Protoplanetary Discs

© Henning & Semenov (2013)
main papers: Woitke, Kamp, Thi (2009), Kamp et al. (2010), Thi et al. (2011), Woitke et al. (2016)

- **stellar parameters**
- **2D hydrostatic disc structure**
- **UV & X-ray irradiation**
  (from star and ISM)
- **dust/gas, grain material, opacities**
- **dust size distribution, settling**
- **detailed continuum RT** → $T_{\text{dust}}(r,z)$
- **kinetic chemistry & ice formation**
- **non-LTE gas heating/cooling**
  → chemical composition, $T_{\text{gas}}(r,z)$
- **prediction of observations**
  → spectral energy distribution (SED)
  → continuum images, visibilities
  → line fluxes IR – mm
  → line velo-profiles, channel maps
ProDiMo: example disc modelling results
Charged grain chemistry

\[ Z + h\nu \rightarrow Z^+ + e^- \]  
photoelectric / photodetachment

\[ Z + e^- \rightarrow Z^- \]  
electron attachment

\[ Z + A^+ \rightarrow Z^+ + A \]  
charge exchange

\[ Z + AB^+ \rightarrow Z^+ + A + B \]  
dissociative charge exchange

\[ Z \rightarrow Z^+ + e^- \]  
thermionic emission

\[ Z + M \rightarrow Z^+ + e^- + M \]  
collisional electron detachment

\[ Z + Z \rightarrow Z^+ + Z^- \]  
tribo-electric changing (missing)

\[ \text{included species} \]
\[ Z^{\ldots}, Z^{\ldots\ldots}, Z^{\ldots\ldots\ldots}, Z, \]
\[ Z^+, Z^{++}, Z^{+++}, Z^{++++} \]

new: charge moments

\[ [Z^+] = n_d \sum_{l=1}^{Z_{\text{max}}} Z_d f(Z_d) \]
<table>
<thead>
<tr>
<th>charge carriers</th>
<th>dusty plasma</th>
<th>dust in dead zone</th>
<th>dust in insulating gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>electron concentration</td>
<td>$n_{el} \approx n_{ions} \gg n_{dust}^+, n_{dust}^-$</td>
<td>$n_{dust}^- \approx n_{ions} \gg n_{el}$</td>
<td>$n_{dust}^- \approx n_{dust}^+ \gg n_{el}, n_{ions}$</td>
</tr>
<tr>
<td>dust motions can build up an electric field?</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>
GGchem: chemical Equilibrium in the Gas Phase

\[
\frac{p_{A_a B_b C_c}}{p^e} = \left( \frac{p_A}{p^e} \right)^a \left( \frac{p_B}{p^e} \right)^b \left( \frac{p_C}{p^e} \right)^c \exp \left( -\frac{\Delta G_f^\circ}{RT} \right)
\]

result:

\[ n_{\text{mol}} = n_{\text{mol}} (p, T, \varepsilon_k) \]

minimisation of system

Gibbs free energy

\[ \Delta G_f^\circ = G^\circ (A_a B_b C_c, T) - a G^\circ (A, T) - b G^\circ (B, T) - c G^\circ (C, T) \]

solution of Guldberg's law of mass action

atom partial pressures

elements

molecule \[ A_a B_b C_c \]

stoichiometric factors
Equilibrium condensation (phase equilibrium)

\[ S_j \begin{cases} < 1 \quad \text{condensate is unstable and not present,} \\ = 1 \quad \text{condensate is stable and present,} \end{cases} \]

Species stable as free a molecule

\[ S_j = \frac{p_j}{p_j^{\text{vap}}(T)} \]

\[ p_j^{\text{vap}}(T) = p^\circ \exp \left( \frac{G^\circ(j[\text{cond}], T) - G^\circ(j, T)}{RT} \right) \]

Molecule does not exist

\[ S_{A_aB^bC_c} = \left( \frac{p_A}{p^\circ} \right)^a \left( \frac{p_B}{p^\circ} \right)^b \left( \frac{p_C}{p^\circ} \right)^c \exp \left( -\frac{\Delta G^\circ_f}{RT} \right) \]

\[ \Delta G^\circ_f = G^\circ(A_aB^bC_c[\text{cond}], T) - a G^\circ(A, T) - b G^\circ(B, T) - c G^\circ(C, T) \]

\[ n_{\text{cond}} = n_{\text{cond}}(p, T, \varepsilon_k^0) \]

\[ \varepsilon_k = \varepsilon_k^0 - \varepsilon_k^{\text{cond}} \]

\[ n_{\text{mol}} = n_{\text{mol}}(p, T, \varepsilon_k) \]

Supersaturation ratios & selection of condensates

Computation of gas-phase chem. equil.
The GGchem code

- up to 40 elements (H, … , Zr, and W)
- up to 1155 molecules
- up to 251 condensates (solids & liquids) from NIST-JANAF and SUPCRTBL
- customised selection of elements, molecules, and condensates
- thermo-chemical data down to 100 K carefully checked
- ultra-fast Fortran code, about 40 ms / call for K=24 elements, scales \( \sim K^3 \)
  - stable iterative solution scheme based on Newton-Raphson
  - fast real*8 (T > 1000 K) and stable real*16 (T→100 K)
- benchmarked against TEA code (Blecic 2016)
- optionally include ions and free electrons, condensates
- specify gas density \((\rho,T)\) or gas pressure \((p,T)\)


→ public code: https://github.com/pw31/GGchem
  > git clone https://github.com/pw31/GGchem
  (includes all thermo-chemical data)
Astro-Chemistry

Geology

gas

condensates

gas

condensates
Classification of exoplanet atmospheres based on H-C-N-O abundances

Fig. 1. Molecular particle concentrations in chemical equilibrium as function of hydrogen, carbon, and oxygen element abundances, calculated for $T = 400$ K and $p = 1$ bar. The central gray triangle marks the region within which H$_2$O, CH$_4$ and CO$_2$ coexist in chemical equilibrium. The dashed lines indicate where the concentrations of two molecules are equal: H$_2$O and CO$_2$, CO$_2$ and CH$_4$, and CH$_4$ and H$_2$O. Blank regions have concentrations < $10^{-4}$. In order to enhance the colour contrasts, a colourmap was chosen that is linear in $(n/n_{\text{tot}})^{1/2}$ from 0.01 to 1.
Table 2. Trace gas concentrations in chemical equilibrium with element abundances $N = 2/13$, $H = 6/13$, $O = 3/13$ and $C = 2/13$, where main constituents are 25% N$_2$, 25% H$_2$O, 25% CO$_2$ and 25% CH$_4$.

<table>
<thead>
<tr>
<th></th>
<th>200 K</th>
<th>300 K</th>
<th>400 K</th>
<th>500 K</th>
<th>600 K</th>
<th>700 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>2 ppb</td>
<td>5.8 ppm</td>
<td>390 ppm</td>
<td>0.52%</td>
<td>2.9%</td>
<td>9.5%</td>
</tr>
<tr>
<td>CO</td>
<td>&lt; 1 ppb</td>
<td>&lt; 1 ppb</td>
<td>260 ppb</td>
<td>39 ppm</td>
<td>0.11%</td>
<td>1.2%</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>205 ppb</td>
<td>4.7 ppm</td>
<td>23 ppm</td>
<td>58 ppm</td>
<td>101 ppm</td>
<td>130 ppm</td>
</tr>
</tbody>
</table>

→ very pure gas at low temperatures
→ effect of mixing entropy with increasing temperature
Fig. 2. Impact of liquid water (H$_2$O) and graphite (C) condensation. The blue and orange contour lines mark where the supersaturation ratio equals one for water and graphite, respectively, at selected temperatures. Inside of the light blue and light orange shaded regions, the gas is supersaturated with respect to water at 350 K and graphite at 500 K, respectively. For higher temperatures, the shaded areas shrink and eventually vanish. The atmospheric compositions of Earth, Mars, Venus, Jupiter and Titan are marked. Earth (assuming 1.5% water content) sits right on top of the $S(\text{H}_2\text{O}, 300 \text{ K}) = 1$ line. A constant pressure of $p = 1$ bar is assumed.
Equilibrium condensation models

**type A:** H$_2$-containing atmospheres made of CH$_4$, H$_2$O and NH$_3$, but no CO$_2$ and no O$_2$.

**type B:** O$_2$-containing atmospheres made of N$_2$, CO$_2$ and H$_2$O, but no CH$_4$ and no NH$_3$.

**type C:** Atmospheres made of H$_2$O, CO$_2$, CH$_4$ and N$_2$, but no H$_2$, no O$_2$ and no NH$_3$.

Type C exoplanet atmospheres are not found in the solar system, however, slightly warmer exoplanets may well host such atmospheres.

The equilibrium condensation models show that type C atmospheres can naturally be created by the outgassing from common rock materials such as carbonaceous chondrites (CI)

CI = Carbonaceous Chondrites
MORB = Mid Oceanic Ridge Basalt
CC = Continental Crust,
BSE = Bulk Silicate Earth
PWD = Polluted White Dwarf observations.

The points where the trajectories start to have graphite are marked by crosses, and the points where liquid water starts to occur are marked by squares.
Summary & Conclusions

- $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{CH}_4$, $\text{N}_2$ are the thermodynamically most favourable molecules in the H – C – N – O system at low temperatures.

- In chemical equilibrium, we find 3 types of atmospheres 200K – 600K:
  - **type A:** $\text{H}_2$, $\text{H}_2\text{O}$, $\text{CH}_4$, $\text{NH}_3$, $\text{N}_2$ – but no $\text{CO}_2$, no $\text{O}_2$.
  - **type B:** $\text{O}_2$, $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{N}_2$ – but no $\text{CH}_4$, no $\text{H}_2$, no $\text{NH}_3$.
  - **type C:** $\text{H}_2\text{O}$, $\text{CH}_4$, $\text{CO}_2$, $\text{N}_2$ – but no $\text{H}_2$, no $\text{O}_2$, no $\text{NH}_3$.

- **%-molecules are in chemical equilibrium:** Their concentrations are constrained by stoichiometry & element abundances – only the identification of what are the most stable molecules must be correct.

- **non-equilibrium markers:**
  - A combination of (i) a molecule that reacts exothermic with one of (ii) $\text{H}_2\text{O}$, $\text{CH}_4$ or $\text{CO}_2$ – both need to be detected simultaneously.

- **a biosignature** should be a non-equilibrium marker. Krissansen-Totton+2019 proposed $\text{CH}_4$ and $\text{CO}_2$ without $\text{CO}$. This works well in type A and type B atmospheres, but it does not work in type C atmospheres, likely producing many false positives.