Gas and Condensation Chemistry in Astronomical Environments

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Outgassing Processes Workshop
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Overview

Dust & Gas in Astronomical Environments

Condensation Chemistry
Calculation
Examples: Solar Nebula,
Clouds in (sub)stellar objects,
Stellar Outflows (circumstellar shells, AGB)

Gas and dust chemistry important in many astronomical environments

For condensation/evaporation modelling major variables are:
overall elemental composition
temperature, pressure/density
gravitational effects; settling
Thermochemical vs. photochemical effects
kinetic effects
Quality of atomic/molecular parameters for thermodynamics, kinetics, photochemistry
Gas and Dust in Astronomical Environments

- **Galaxies** – Dust Lanes
  - Inter-Galactic & Interstellar Media (IGM, ISM)

- **Circumstellar Environments**
  - Star-forming Regions:
  - Proto-stellar & Planetary Accretion Disks
  - Dying Stars, Late-type/Evolved Stars:
    - AGB, PNe, SNe Ia, II; Release of elements

- **Main-Sequence of Stars**
  - Massive Stars (O, B, A) → Vega-type Debris Disks
  - Brown Dwarfs & Low-Mass Stars (M, L, T, Y) → Clouds

- **(Exo)-Planetary Systems**:
  - Planets, Moons, Asteroids, Comets, Meteorites,
    - Interplanetary Medium (Zodiacal Light)

- **Planetary/Solid Objects Environments**
  - Atmospheres: Cloud-layer(s), Hazes, Aerosols
  - Surfaces: Hot & Cryo-Volcanism; Impact vaporization
Ly-α absorption of neutral H-rich regions seen in spectra of background quasars (distant Active Galactic Nuclei) at early galaxy-forming times (at high redshift $2 < z < 5$)

Mass density of neutral gas in DLAs is similar to mass density of stars found in galaxies today so DLAs are a measure of neutral matter for star formation in galaxies

Metal absorption lines: alpha elements made in core-collapse SNe II: Si and S
Fe-peak elements preferentially made in SN Ia: Fe and Zn

**Elements made by same processes typically have similar relative abundances as seen in sun**

But often found $\text{Si/S} < (\text{Si/S})_{\text{sun}}$ and $\text{(Fe/Zn)} < (\text{Fe/Zn})_{\text{sun}}$

Gas has volatile S and Zn but less Si and Fe $\rightarrow$ dust prolific in early galaxies & IGM

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**Probing the Intergalactic Medium (IGM)**

Distant quasar

Damped Lyman alpha (DLA) systems

Cloud at high redshift

Cloud at low redshift

Composite Absorption spectrum
The Andromeda Galaxy shown in the far-infrared (left) and visible (right), with a composite image in the middle. *Image credit: Robert Gendler*(visible) ; *ESA / Herschel / SPIRE / HELGA* (far-infrared).
The Andromeda Galaxy from visible to far-infrared with a composite image in the middle. 

*Image credit: Robert Gendler (visible); ESA / Herschel / SPIRE / HELGA (far-infrared).*
Studying the stars in the laboratory: A distant planetary nebula and a SiC grain isolated from meteorites that formed in such an environment.
Genuine Star Dust in Meteorites

- Nano-diamonds
- SiC
- MgAl₂O₄
- Graphite with internal carbides
- SiC in matrix

500 nm graphitic layers

M. Amari
R. S. Lewis
T. Bernatowicz
S. Amari
C. Croat
R. S. Lewis
S. Amari
L. A. Nittler
A. M. Nguyen
Vega-type debris disks

Proto Type System Vega (α-Lyr), A0V star, 2.1 \( M_{\odot} \)

Stars with debris-disks, dust revealed by infrared excess emission to stellar radiation

- Dust from collisions of smaller objects in a planetary disk akin to Kuiper-Edgeworth belt in our solar system
- Remnant disk formed when stellar/planetary system formed
- Objects still dynamically active, need ongoing collisions to make dust
- Mechanical dust processing; impact heating effects akin seen in meteorites?
- Need very energetic events for evaporation; any signatures for recondensation of “fresh dust”? 
**Inputs to Chemical Equilibrium Computations**

**Elemental Abundances**
- for solar, see Palme, Lodders & Jones, 2014, Treatise on Geochemistry; Lodders, Palme, & Gail 2009, Landolt Boernstein

**Temperature, Pressure/Density of System**
- Adiabats (Solar nebula, planetary accretion disks, planetary atmospheres, circumstellar outflows...)
- Representative total pressure of system for studying relative stability trends

**Thermodynamic Properties/Equations of State**
- *Self-consistent set* of heats of formation, entropies, heat capacities as function of temperature for pure solid, liquid, and gaseous substances (e.g., Janaf Tables, Gurvich et al., primary literature); solid-solution properties/activity coefficients for trace elements dissolving in major mineral host phases, non-ideal fugacity coefficients for gases at high total pressures & near critical points.

**Reliable Code**
- Gibbs-energy minimization codes (may not converge & run into local minima; number of possible coexisting phases may be limited to a few; may not return mass-balance.
- Equilibrium-constant/Mass-action codes
Proto-Planetary Disks

Radial Distance (AU)

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Temperature (K)

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Pressure (bar)

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Thermochemistry vs. Photochemistry >>
Example Condensation & Evaporation:

Fe (g) = Fe (s)

For condensation: \( a_{Fe} = 1 = K P_{Fe} = K P_{vap} \)

or \( P_{Fe} = P_{vap} \)

Partial pressure of monatomic Fe must equal monatomic Fe saturation vapor pressure over pure solid or liquid Fe.

At thermodynamic equilibrium: \( K = a_{Fe} / P_{Fe} = a_{Fe} / X_{Fe} P_{tot} \)

\( K \) = equilibrium constant, \( T \)-dependent

\( a = \) thermochemical activity of solid or liquid, \( a \equiv 1 \) for pure substance;

\( a_{Fe} = 1 \) is the requirement for condensation.

\( P_{Fe} = \) partial pressure of condensing gas (here monatomic Fe)

\( P_{Fe} = X_{Fe} P_{tot} \)

\( X_{Fe} = \) mole fraction of condensing gas in gas phase; follows from overall composition, \( X_{Fe} = \frac{Fe \text{ atoms}}{(\Sigma \text{all other atoms + molecules in gas})} \)

\( P_{tot} = \) total gas pressure of system; usually given/assumed

For \( a_{Fe} = 1 \), \( K \) is just the inverse of the saturation vapor pressure for iron gas: \( K = 1 / P_{vap} \)

Saturation Ratio: \( S = P_{Fe} / P_{vap,Fe} = 1 \) at equilibrium

Kinetic inhibition may require super-saturation \( S > 1 \) for condensation.
Iron Condensation at 1 bar

- 1793 K, 50% Fe condensed
- 1843 K, Fe condensation starts

Iron Distribution at 1 bar

- Fe-metal alloy
- FeS
- Fe,P
- gases: Fe, FeH, ...
Corundum Condensation -- see Lodders 2003 for details

$$2\text{Al} (g) + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 (s) + 3\text{H}_2 (g)$$

$$\log K_{eq} (T) = \log a_{\text{Al}_2\text{O}_3} + 3 \log X_{\text{H}_2} - 2 \log X_{\text{Al}} - 3 \log X_{\text{H}_2\text{O}} - 2 \log P_{\text{tot}}$$

$$= A + B/T$$

** Find $K_{eq} (T)$ data

** Calculate the $X_{\text{Al}}$ the from gas chemistry for all elements and gases

for given $T$ and $P_{\text{tot}}$ equilibrium AND mass-balance

** also calculate corundum activity with $K_{eq}$

** Find solution where $a_{\text{Al}_2\text{O}_3} = 1$

$$P_{\text{Al}} = P_{\text{tot}} X_{\text{Al}}$$ and approx. $$X_{\text{Al}} \approx P_{\text{Al}}/(P_{\text{H}_2} + P_{\text{He}}) = P_{\text{Al}}/(A_{\text{H}}/2 + A_{\text{He}})$$

where $A_i = \text{abundance}$

Set $P_{\text{Al}} \approx A_{\text{Al}}$ ONLY IF $P_{\text{Al}}$ is the major/only Al-bearing gas

– but lots of abundant Al-gases Al, AlO, HAlO, Al$_2$O…
Solar Composition System: Condensation/Evaporation Sequence

Ca-Al-Ti oxides

Change in sequence
Above ~10^{-4} bar, **metal alloy** before **Mg-silicates**

High-T phases > 600 K in solar composition make ~0.5% of total mass

Troilite (FeS)

FeO into silicates: higher H_2O/H_2 ratio or higher dust/gas ratios

**Magnetite, Hydrated silicates, e.g** talc → **KINETICS**

Water Ice
~ 130 – 180 K
Start with Solar system **elemental abundances**
(e.g., Palme, Lodders, Jones 2014, Treatise of Geochemistry)

Chemical & physical fractionation

*** of compounds *in the accretion disk*
Condensation & Evaporation, Phase Stabilities \( f(T,P,r,z,t) \)
Dynamical & Density Sorting (gravity), Radial Mixing (ices)
\( \rightarrow \) feed-back into disk structure (opacity, redox state)

**** of planet-building blocks
Thermal stabilities of solids and liquids (volatile retention)
Iron oxidation/reduction reactions (metal content)
Extent of gas-solid equilibria at low temperatures,
e.g., sulfides, hydrated silicates
gas giant planets also \( \text{H}_2 \) & \( \text{He} \) gas accretion efficiencies with time

***** *fractionations after dissipation of the gaseous disk*
Outgassing, impact processing (Moon), debris disks
Major components for solar composition

**Gases** $H_2$, He not condensing

**Rock:** Metal, Silicate, Sulfide(s). Trace element into solid-solution(s).

**Ices:** $H_2O$; CO, $CH_4$, $CO_2$, $NH_3$, $N_2$, and/or clathrates or hydrates thereof also noble-gas clathrates

Methane Clathrate:
- **Methane** is a guest molecule
- **Water molecules** form a cage through H-bond bridging.

ice composition very dependent on kinetics

Conversion of CO (gas) to $CH_4$ (gas); $N_2$ (gas) to $NH_3$ (gas)
approximate rock & ice masses in a planetary accretion disk of solar composition assuming equilibrium

approximate rock & ice masses in a planetary accretion disk of solar composition assuming equilibrium

But: not all low-T phases can form within the solar nebula lifetime

No hydration of silicates in “vacuum”; only little methane gas, little ammonia gas
Non-equilibrium condensate mass distribution
Half of all C in condensed organics

ISM-organics require 350-450 K for complete evaporation, Nakano et al. 2003

Solid organics could be important for core accretion model, Lodders 2004, ApJ

No hydrous silicates, no methane and ammonia bearing ices
Condensation and Evaporation: Kinetic inhibition may require super-saturation to initiate condensate formation

Homogeneous condensation: Condensate forms directly from gas phase; refractory phases observed in presolar grains

Heterogeneous condensation: Condensate grows onto existing grains; nucleation seeds

Grain growth: Deposition, coalescence, coagulation

Combine observed phase info & calculations to find overall composition and physical conditions ($T,P$) of the condensate source
Do Equilibrium Calculations Apply?

Application of equilibrium condensation calculations is supported experimentally.

Condensation experiments at high T and low total pressure (1000-1285K, ~0.004 bar) yield many expected condensates in crystalline form; steady-state attained within an hour.

Equilibrium thermodynamics also explains presolar grain mineralogy and their trace element contents. They formed in low pressure winds of giant stars, so eq. thermo. should work well in high P atmospheres.

Laboratory condensation of refractory dust in protosolar and circumstellar conditions

Alice Toppani a,b,*, Guy Libourel a,c, François Robert b, Jaafar Ghanbaja d

Gases at low-pressure. Our experimental results show that high-temperature condensation of multi-elemental refractory gases (“Mg–Si-rich” and An50Di50) at ~4 × 10^{-3} bar results in direct formation of crystalline grains, that condense either directly in the gas or on the Pt-grid. The condensation of amorphous phases with stochastic composition is thus not favored.

The mineralogy of the condensed crystals, close to that predicted by equilibrium thermodynamic calculations, varies with temperature and duration of the condensation experiments. We have shown that chemical reactions between gas and condensates are rapid enough to attain a steady state on a relatively short period of time (~1 h at ~4 × 10^{-3} bar). Furthermore, high-temperature condensation results in chemical fractionation of the gas, i.e. depletion in refractory elements at high-temperature. This indicates that equilibrium conditions may not be achieved in this regime.
Proto-Planetary Disk

Dust Formation
(1) Condensates from gas  (2) Gas-grain reactions

Fe-metal $\rightarrow$ FeS; sulfur removal

corundum $\rightarrow$ gehlenite $\rightarrow$ feldspar; Na, K removal
Cloud layer

High T
High P
deeper 
hotter 
denser
S into FeS (troilite)  
NH₄SH

P into Fe₃P (schreibersite)  
NH₄H₂PO₄

Na, K into feldspar  
Na₂S, KCl

"proto planetary disk condensates"  
"cloudy atmosphere condensates"
Dotted line at ~1300K, ~10 bar for Na (and also K) removal into feldspar in solar nebula
But in brown dwarfs, need lower T for Na and K removal by Na₂S & KCl condensation
An astronomer’s summary about potassium condensation in brown dwarfs:

... . If elements such as Al, Ca, and Si were not lost via such condensate-cloud formation at higher temperatures, neutral potassium would not have been seen as a major absorber in late-L and T dwarfs because it would have been removed by silicate condensates like orthoclase (KAlSi₃O₈, ...). Such is the bizarre and intricate dance of the condensates in M, L, and T dwarf atmospheres. For more information on this topic, the reader is referred to the detailed papers by Lodders (2002) and Lodders & Fegley (2002) and the review by Burrows et al. (2001)
Hot Exoplanets – Rock Vapor Atmospheres

• Most terrestrial accretion theories suggest that the Earth was at least partially molten
  – Many accretion models suggest presence of magma ocean

• Giant impacts, e.g. Moon-forming impact generate magma oceans which are hot enough to vaporize
  – evidence for large impacts in exo-planetary systems (Song et al., 2006, Nature)

• Terrestrial-type planets should get hot (T > 2000 K) and vaporize during accretion
  – Vaporization generates silicate atmospheres containing gases such as SiO that may be detectable spectroscopically
Core – Accretion Model Gas Giant Planets

Fast build-up of protocore facilitated if surface mass density in disk is increased need up to 5-10 times the rock surface density (Lissauer, 1987, Pollack et al. 1996, Hueso & Guillot 2003)

Water Ice: Mass density of solids higher at the snowline and beyond

Solar abundances allow for factor 2-3 mass increase
2014: rock ~ 0.5% and water ice ~ 0.6% of all mass
AG89: rock ~ 0.5% and water ice ~ 0.9% of all mass

Diffusive redistribution of water from inner solar system and ice cold-trapping at the snow line and beyond can increase mass density (Stevenson & Lunine 1988, Cyr et al. 1998)

If Jupiter formed with a lot of water ice: Where is the water now?
The Tar-line
Carbonaceous condensation/evaporation front

Organic solids more stable than water ice during condensation and more stable against evaporation

Carbonaceous matter is more refractory than water
Gooey sticky properties

Jupiter’s observed envelope composition
high carbon abundance: C/H ~ 3-4x solar
low-solar oxygen: O/H = 0.5 – 1 x solar

Compared to methane, water abundances increase more strongly from Jupiter to Uranus suggesting water ice pile-up in the outer solar system.
Overall Composition Matters!

Condensation temperatures for solar composition may only apply to H and He-rich systems with similar metallicity and C/O ratios!

Types of condensates and sequence of their appearance as function of T depend on total pressure and overall composition.

An increase of C/O in a gas of otherwise solar composition changes condensates of many elements from oxides and metals to carbides, nitrides, sulfides, and silicidies.

A decrease in hydrogen (increase of metallicity) in an otherwise solar composition gas makes the gas more oxidizing and favors oxide stabilities.

Essentially hydrogen-gas free systems at high temperatures (silicate magma oceans, volcanic gases) have different gas species coexisting than “astronomical condensates” in a H, He rich gas.

Condensate phases will also depend on the relative amounts of sulfur, nitrogen, halogens depending on the overall fractionation/differentiation history of the system under consideration.
Inner Circumstellar Chemistry of Red Giant Stars

Condensate mineral is determined by C/O

M stars, C/O <1 oxides, silicates, metal

C stars, C/O >1 graphite, carbides, nitrides, sulfides, silicides

Several of these minerals observed in CSE and among presolar grains

10^{-5} bar; C/O > 1, MgS at 1030K
In the CSE, densities drop more than ten orders of magnitude. Temperature also drop steeply in the CSE.

Photospheric equilibria become quenched as required reaction timescales become larger than expansion timescales.

Outermost CSE receives interstellar UV \( \rightarrow \) photochemistry
Circumstellar Envelope Chemistry of Red Giant Stars

Photospheric and inner shell region: At a given distance $R$, equilibrium is reached if reaction times are shorter than expansion timescales

$$\tau_{\text{chem}}(R) < \tau_{\text{expand}}(R)$$

Thermochemical equilibrium abundances become frozen in at distances where

$$\tau_{\text{chem}}(R) = \tau_{\text{expand}}(R)$$

Different reactions have different quench distances. Endothermic reactions and reactions with high activation energies quench closer to the star than exothermic reactions, e.g., CO, SiO, SiS, HCN difficult to destroy at low temperatures and pressures

Models require kinetic reaction networks
Observed Circumstellar Chemistry of the Carbon-rich Giant Star IRC+10216

Observed abundances consistent with quenched photospheric equilibrium abundances

Abundances higher than expected from equilibrium at given R, also higher than quenched equilibria from closer-in; grain-surface reactions? Remains a mystery

Photochemically produced radicals and molecules; any dust destruction?

Summary

Astronomical environments display huge diversity in Dust & Gas Inventories over time and in physical settings

Condensation Chemistry
Calculations are useful to model observations
Examples: Solar Nebula,
Clouds in (sub)stellar objects,
Stellar Outflows (circumstellar shells, AGB)

Major dependencies for condensation/evaporation modelling:
overall elemental composition
temperature, pressure/density
gravitational effects; settling
thermochemical vs. photochemical effects
kinetic effects
Quality of atomic/molecular parameters for thermodynamics,
kinetics, photochemistry