Evolutionary Stages and Issues

- infall onto disk
  - accretion shock
  - irradiation of infalling gas/dust

  <u>what survives intact?</u>

- Disk accretion stage
  - strong thermal and pressure gradient in nebula
  - dust properties are evolving
  - accretion rate is variable with gradual decline – UV emission
  - turbulent disk: mixing both radially and vertically

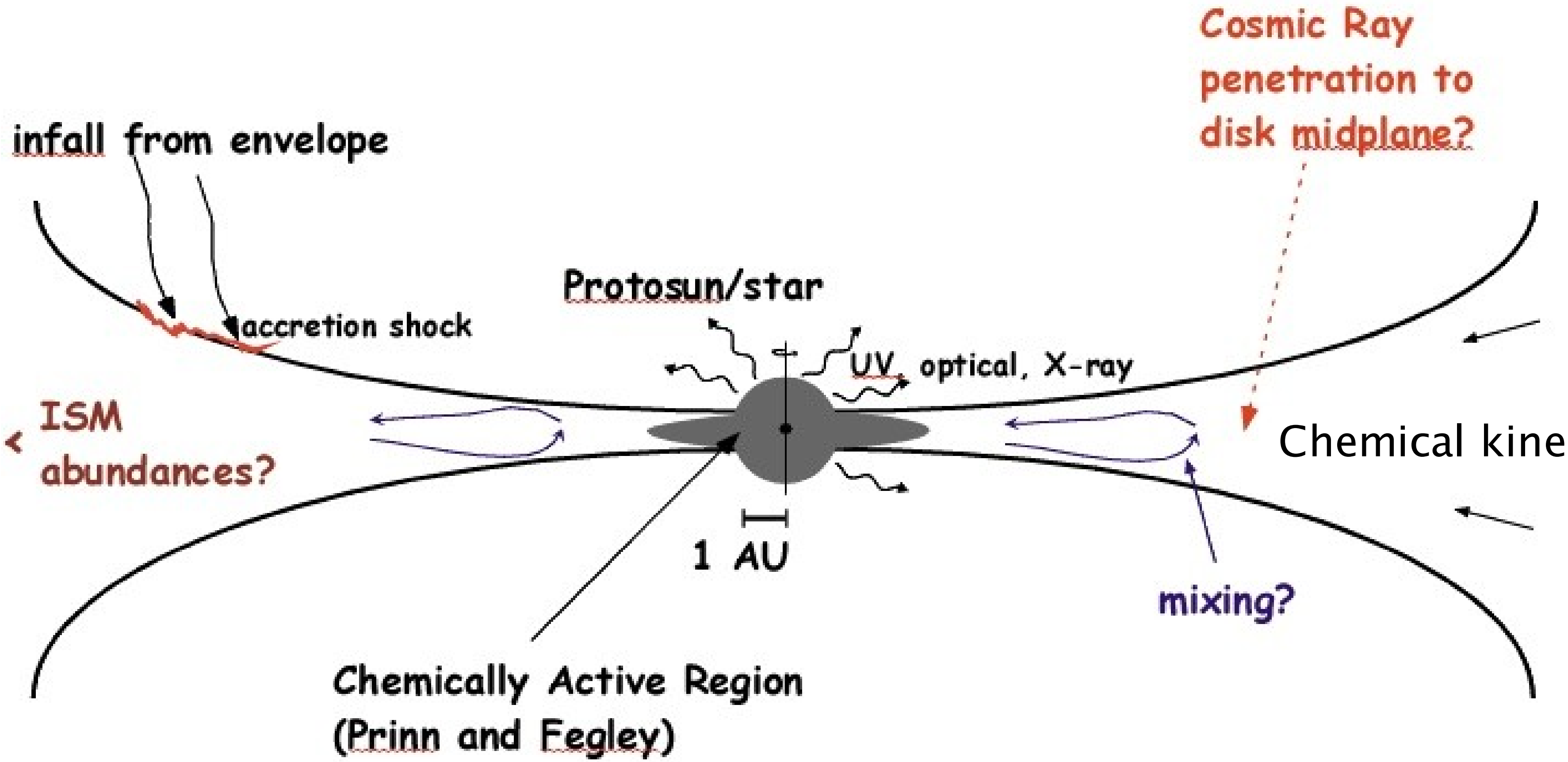
  <u>how does this alter the chemistry? are there detectable trends?</u>

- Planet formation and disk gas clearing
  - proto-Jovian nebula forming in a disk

  <u>how is the chemistry of these regions characterized?</u>

Disclaimer: my aim is to provide basic tools (microphysics)
-- may not answer any of these questions!

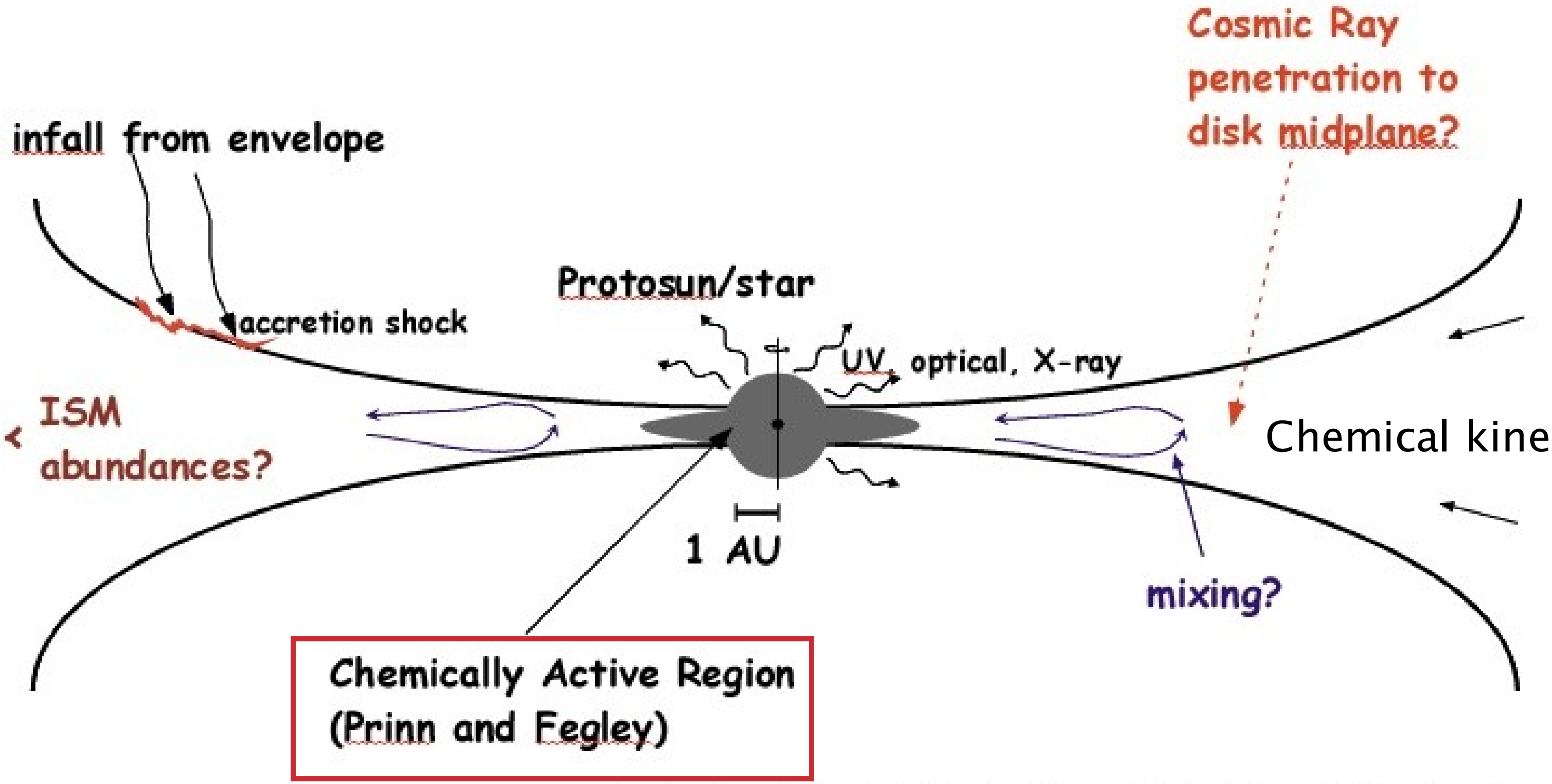
Disk Chemistry



Chemical kinetics

after Lunine 1997, Origins of Life and Evolution of the Biosphere ed D.C.B. Whittet, 27, 205

Disk Chemistry



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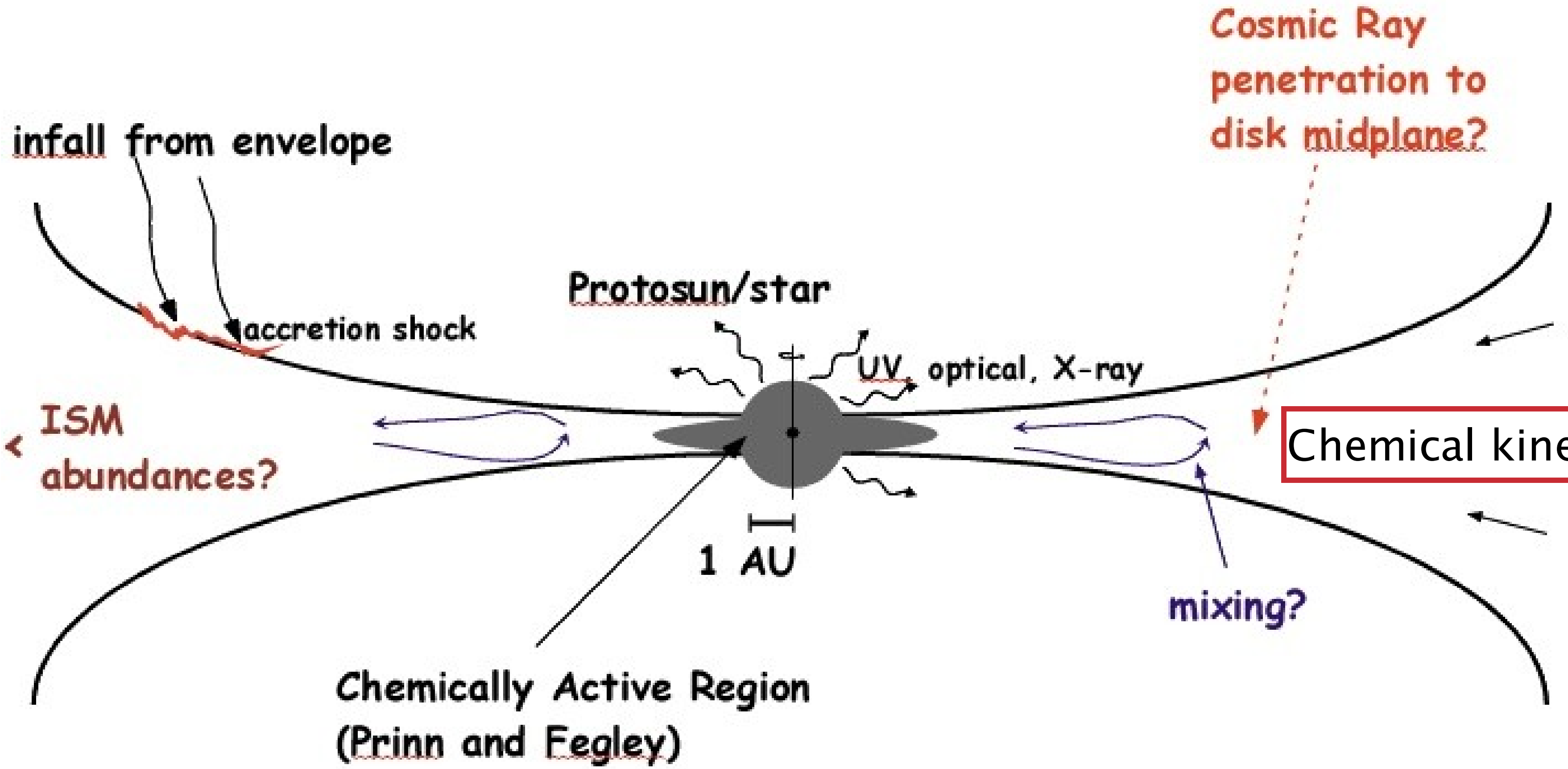
Disk Chemistry



Chemical kinetics

after Lunine 1997, Origins of Life and Evolution of the Biosphere ed D.C.B. Whittet, 27, 205

Thermochemical Equilibrium

- Also listed as thermodynamical equilibrium
- Defined as the state of maximum entropy or, the state of minimum Gibbs free energy of system.
  - state towards which all chemical systems are being driven
- “One way to look at this is it is the final composition that would result from a system if one waited forever and a day” (S. Buckley, UCSD)
  - resulting composition does not depend on initial state
  - given pressure (P) and temperature (T) one can predict the chemical composition
- Commonly used in stellar atmosphere calculations, brown dwarf and extra-solar planet atmospheres -- and initially in the solar nebula.

Thermochemical Equilibrium

- key references
  - Lewis 1972, Icarus, 16, 241
  - Lewis 1974, Science, 186, 440
  - Barshay and Lewis, 1976, ARAA, 14, 81
  - Lewis and Prinn, 1980, ApJ, 238, 357
  - Prinn and Fegley, 1981, 249, 308
  - Prinn 1993, PPIII
  - Fegley 1999, Sp. Sci. Rev., 90, 239
  - Sharp and Heubner 1990, ApJS, 72, 417 (with condensation)
  - Burrows and Sharp 1999, ApJ, 512, 843 (Brown Dwarfs…)

Thermochemical Equilibrium

- complications
  - disk systems have finite lifetimes
  - mixing also may limit the time gas spends in a given physical state
    - both of these were noted early on
  - current observations suggest chemistry is not in equilibrium
    - observations do not probe the inner disk!
- where in the disk is thermochemical equilibrium relevant????

Thermodynamic Equilibrium

For every reaction an equilbrium can be defined.
For example in the following reaction:

$$2H + O \rightleftharpoons H_2O$$

the ratio of partial pressures ($p_X = n_X kT$) can be determined from the equilbrium constant $K_p(\mathrm{H_2O})$ (a tabulated quantity: JANAF tables from NIST).

$$K_p(\mathrm{H_2O}) = \frac{p(H_2O)}{p^2(H)p(O)} = exp[-\Delta G^\circ(\mathrm{H_2O})/\mathrm{RT}]$$

Where R is the gas constant and the ΔG is the Gibbs free energy, which is expressed as,

$$\Delta G^\circ(H_2O) = \Delta G_f^\circ(H_2O) - 2\Delta G_f^\circ(H) - \Delta G_f^\circ(O)$$

ΔG_f° is the standard free energy of formation.

Thermochemical Equilibrium

In an system with multiple species with fixed pressure and temperature we can use the equilibrium constants to determine the composition.

Take the following system:

$$CO \rightleftharpoons C + O$$

$$CN \rightleftharpoons C + N$$

We know the following:

$$K_{CO}(T) = \frac{p_c p_o}{p_{co}}$$

$$K_{CN}(T) = \frac{p_c p_n}{p_{cn}}$$

We can define “fictituous pressures”, P_C, P_O, and P_N which can be expressed as:

Thermochemical Equilibrium

$$P_O = p_O + p_{CO} = p_O + \frac{p_C p_O}{K_{CO}}$$

$$P_N = p_N + p_{CN} = p_N + \frac{p_N p_C}{K_{CN}}$$

$$P_C = p_C + p_{CN} + p_{CO} = p_C + \frac{p_C p_N}{K_{CN}} + \frac{p_C p_O}{K_{CO}}$$

and the pressure (mass) balance equation,

$$P = p_C + p_N + p_O + p_{CO} + p_{CN}$$

From these you can solve for the partial pressures and composition.

There are some other more commonly used methods in the literature - which we will examine...

Thermochemical Equilibrium

- often in the meteoritic or planetary literature the term *fugacity* is used – what is it?

Start from the beginning:

$$G = H - TS = E + PV - TS$$

where H is the enthalpy, E the energy, V the volume, and S the entropy.

- For a closed thermodynamic system the equilibrium is attained when G is at a minimum -- note S is therefore at a maximum.

Thermochemical Equilibrium

$$dG = dE + PdV + VdP - TdS - SdT$$

1st law of thermodynamics

$$dG = \cancel{d}E + P\cancel{d}V + VdP - T\cancel{d}S - SdT$$

$$dG = VdP - SdT$$

If this is an ideal gas that $PV = nRT$ and

$$(dG)_T = VdP = \frac{nRT}{P}dP$$

$$G_B - G_A = \int_{p_A}^{p_B} \frac{nRT}{P}dP = nRTln\left(\frac{p_B}{p_A}\right)$$

Thermochemical Equilibrium

If this is an ideal gas that $PV = nRT$ and

$$(dG)_T = VdP = \frac{nRT}{P}dP$$

$$G_B - G_A = \int_{p_A}^{p_B} \frac{nRT}{P}dP = nRTln\left(\frac{p_B}{p_A}\right)$$

What if there are departures from an ideal gas?

$$G_B - G_A = \int_{p_A}^{p_B} \left(V - \frac{nRT}{P}\right)dP + nRTln\left(\frac{p_B}{p_A}\right) = nRTln\left(\frac{f_B}{f_A}\right)$$

f is the fugacity. (Defined on next slide)

Thermochemical Equilibrium

$$G_B - G_A = \int_{p_A}^{p_B} \left(V - \frac{nRT}{P}\right) dP + nRTln\left(\frac{p_B}{p_A}\right) = nRTln\left(\frac{f_B}{f_A}\right)$$

– The fugacity is essentially a pressure term for a non-ideal (real) gas.

– It is equivalent to the partial pressure if the gas is an ideal gas.

Rewrite in terms of some known or measured state (e.g. 1 atm):

$$G_B = G^\circ + nRTln\left(\frac{f_B}{f_0}\right) = G^\circ + nRTln(a)$$

Where a is the activity, which is defined as f/f_0

For an ensemble of atoms and molecules minimize the total Gibbs free energy and determine the composition.

Thermochemical Equilibrium

Now if we have an ensemble of atoms and molecules we can write out the total Gibbs free energy:

$$G = \Sigma n_{i,p}(\Delta G_{i,p} + RTln\, a_{i,p})$$

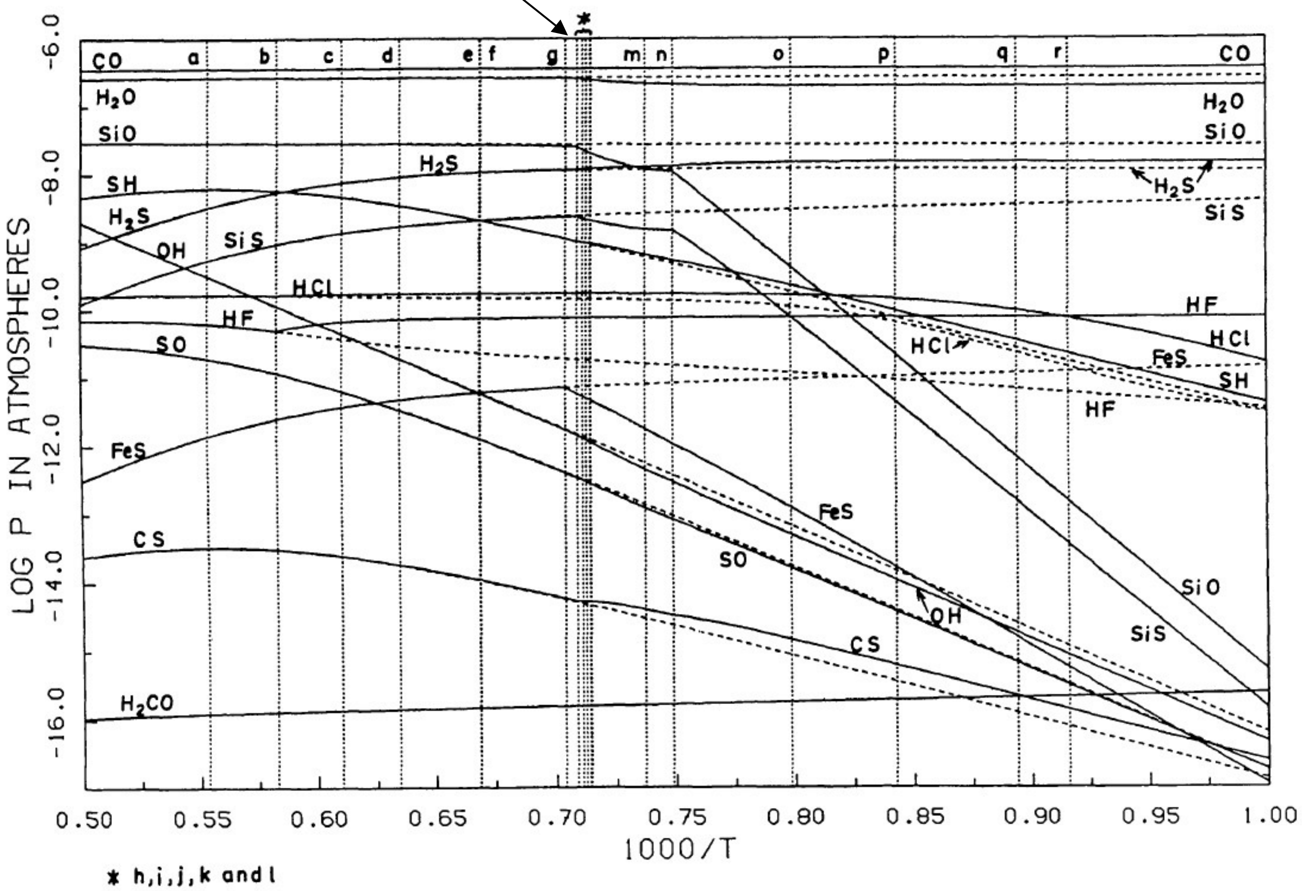
Here n is the number of moles of species i in phase p.

There is one more set of equations detailing mass balance of each element which is normalized to the assumed initial composition.

The total Gibbs free energy is now minimized with the variables being the number of moles of each species – thereby determining the equilibrium condensation!

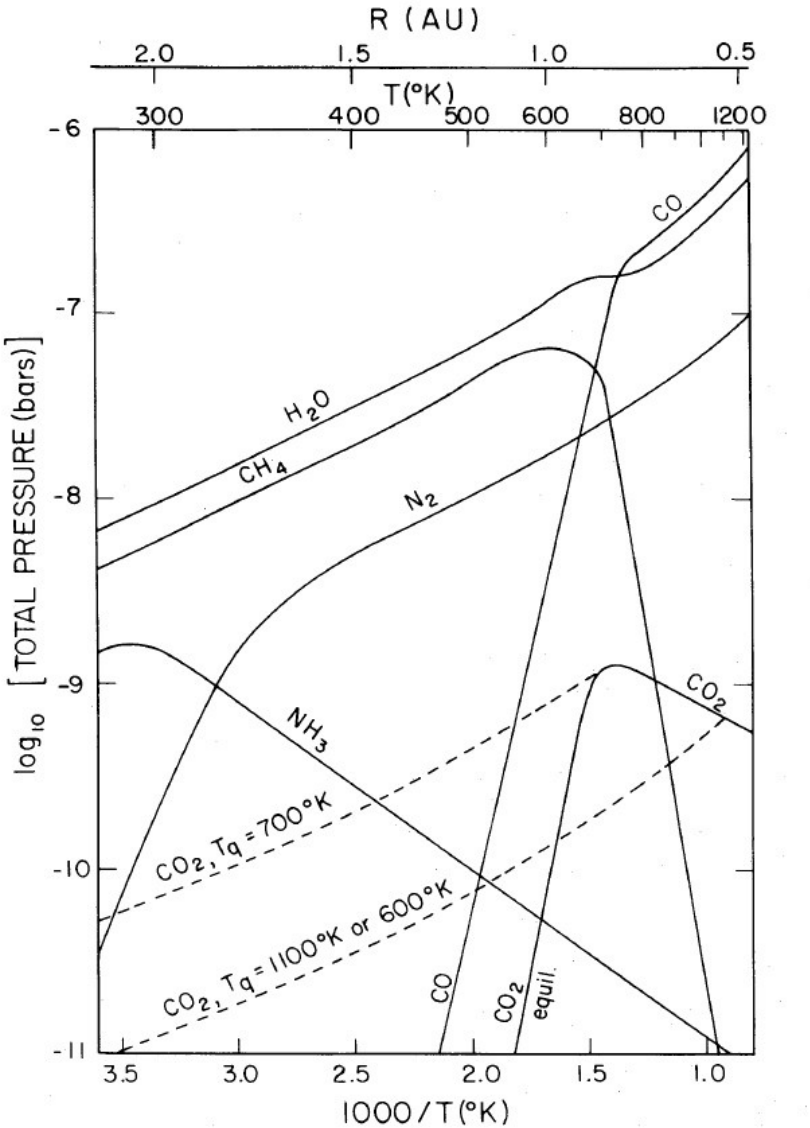
Example: Sharp and Huebner

appearance of Forsterite Mg_2SiO_4



calculations at 5 x 10^{-4} bar -- Jupiter’s atmosphere or ~0.1 AU in the disk

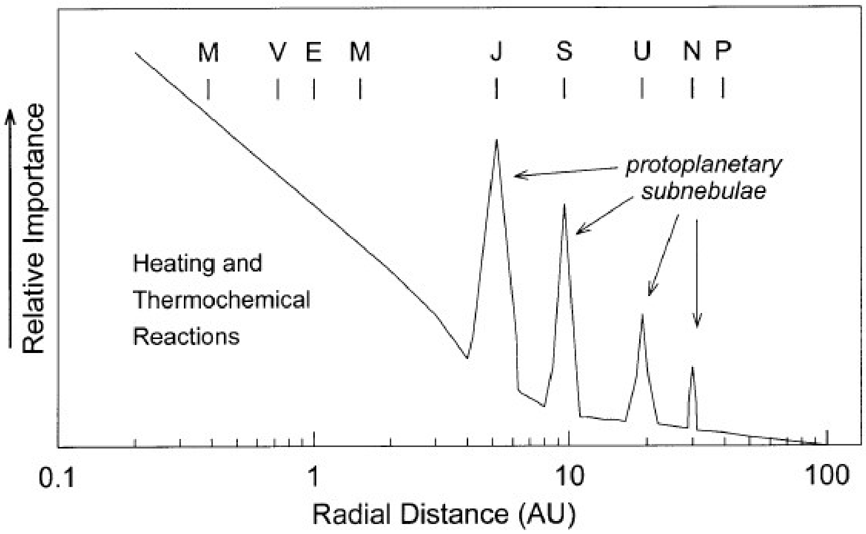
Kinetic Inhibition

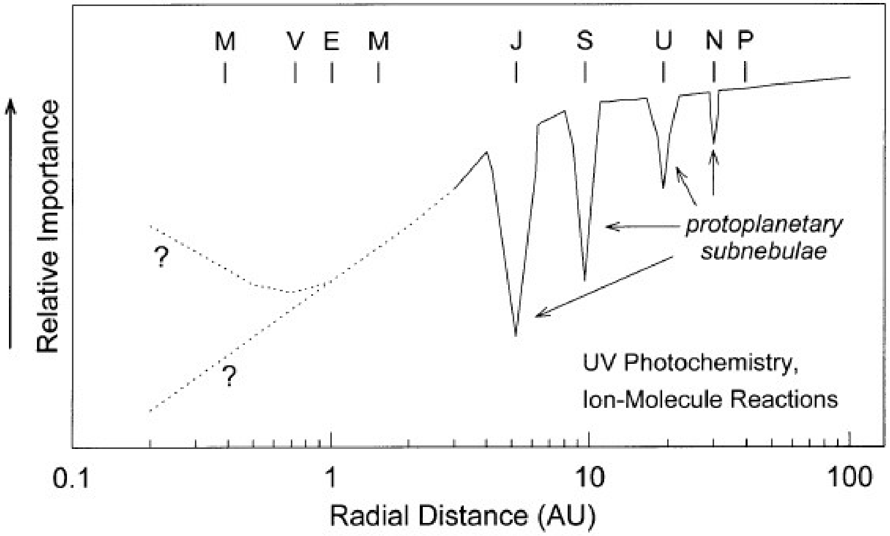


- PPIII: kinetic inhibition widely discussed.
- Lewis and Prinn 1980 – CO and N_2 would be the dominant form of carbon and nitrogen in the nebula.
  - Estimate timescale for mixing in the inner nebula was ~ 5 x 10^7 s
  - conversion from CO to CH_4 at 1000 K is on the order of ~10^{10} s and longer at lower temperature
  - Therefore equilibrium CO conversion is stopped/quenched below 1000 K -- and methane is not formed.
- Prinn and Fegley 1981 – CH_4 and NH_3 dominate in Jovian circumplanetary nebula.
- These types of models explain why certain types of minerals are not found in meteorites.

Where is Thermochem. Eq. relevant?

Fegley 1999





- Likely valid in the inner nebula and in circumplanetary nebula
- The key question is mixing – if there is significant RADIAL mixing then the inner nebula might “contaminate” the outer nebula.
- Also mixing between circumplanetary nebula and surrounding disk could contribute.
  - Prinn and Fegley attributed ratio of CO/CH_4 and N_2/NH_3 in comets to such mixing
  - but ISM ices…
- NOT CLEAR

Kinetic/Nonequilibrium Chemistry

- Enables examination of temporal dependence of gas chemistry
  - At any temperature or pressure
- Particularly useful in low temperature/low pressure regions where thermochemical equilibrium is not valid.
  - This is most of the disk mass!
- Observations and models suggest chemistry is similar to dense regions of the ISM exposed to radiation.
- Complicated --
  - Gas phase chemistry
  - Gas-grain interaction
  - Grain surface chemistry
  - Shifting physical parameters

Gas Phase Ion–Molecule Chemistry

- Based on interstellar chemical networks
  - Herbst (2005), Le Teuff et al. 2000
- Exothermic (T < 100 K)
  - inner disk endothermic reactions or reactions with barriers become active.
- Timescale for 3-body (A + B + M -> AB + M) reactions is long:

  $\tau_{3\text{-body}} \geq 3 \times 10^{23}/n^2$ yr
  - Can be relevant in the disk midplane where $n > 10^9$ cm^{-3} (see Willacy et al. 1998)
- In 1970's Herbst and Klemperer realized that reactions between ions and neutrals are generally exothermic and proceed quickly.

Langevin Rate (from Watson 1976)

Hard collision limit – Langevin rate.
For ion-molecule systems polarization gives the long range potential:

$$V_i = -\epsilon e^2/2r^{-4}$$

ϵ is the polarizability of the neutral.

In neutral-neutral collisions the long range attraction is due to van der Waal's force:

$$V_n \simeq -\epsilon_1 \epsilon_2 I/r^{-6}$$

Rate coefficients from this are:

$$k_i =< \sigma v >= 2\pi \left(\frac{\epsilon e^2}{\mu}\right)^{1/2} \sim 2 \times 10^{-9} \;\; cm^3 \; s^{-1}$$

$$k_n = \pi 13.5 \left(\frac{\epsilon_1 \epsilon_2 I}{\mu}\right)^{1/3} < v^{1/3} >\sim 4 \times 10^{-11} \;\; cm^3 \; s^{-1}$$

Values using typical numbers ($\epsilon = 10^{-24} cm^3$; $I = 1\ Ry$; T = 100 K; $\mu = 2m_H$)

Working Guide (Watson 1976)

- Exothermic neutral–neutral reactions whose rates are near k_n at room temperature are likely to proceed.
  - A laboratory rate below this indicates an activation barrier
- Activation barriers usually occur when a chemically saturated molecule is involved (as a reactant or product)
  - Not likely to occur in reactions involving atoms and radicals
- Exothermic ion–molecule reactions for small molecules usually proceed at *Langevin* rate and are temperature independent (allowed progress)
- BUT low temperature measurements in lab -- particularly for neutral–neutral reactions show some surprises -- caution….

Chemical Reaction Types

Reaction Type	Example	Typical Rate Coefficient
Ion-Neutral	$H_3^+ + CO \rightarrow HCO^+ + H_2$	$\sim 10^{-9}$ cm^3 s^{-1}
Radiative Association	$C^+ + H_2 \rightarrow CH_2^+ + h\nu$	$\sim 10^{-17}$ cm^3 s^{-1}
Neutral Exchange	$O + OH \rightarrow O_2 + O$	$\sim 10^{-11} - 10^{-10}$ cm^3 s^{-1}
Charge Transfer	$C^+ + S \rightarrow S^+ + C$	$\sim 10^{-9}$ cm^3 s^{-1}
Radiative Recombination	$C^+ + e^- \rightarrow C + h\nu$	$\sim 10^{-12}$ cm^3 s^{-1}
Dissociative Recombination	$H_3O^+ + e^- \rightarrow H_2O + H$	$\sim 10^{-6}$ cm^3 s^{-1}
Photoionization	$C + h\nu \rightarrow C^+$	$\sim 10^{-9}e^{-\gamma A_v}$ cm^3 s^{-1}
Photodissociation	$H_2O + h\nu \rightarrow O + OH$	$\sim 10^{-9}e^{-\gamma A_v}$ cm^3 s^{-1}

Generally reaction rates are expressed as $k = k_{300\,K}(T/300\ K)^{\alpha}e^{-\beta/T}$ cm^{3}s^{-1}

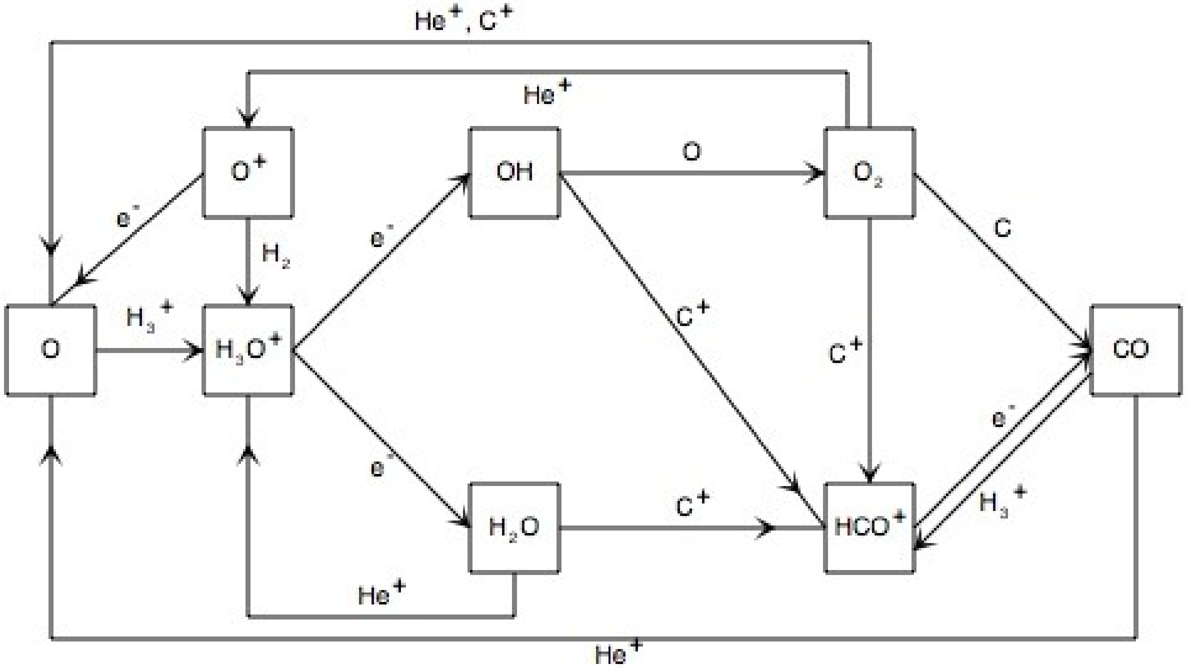
Major issues: most reactions not measured at low T -- o.k. for ion-molecule But neutral-neutral is an issue. Products of dissociative recombination not always known.

Kinetic Chemistry

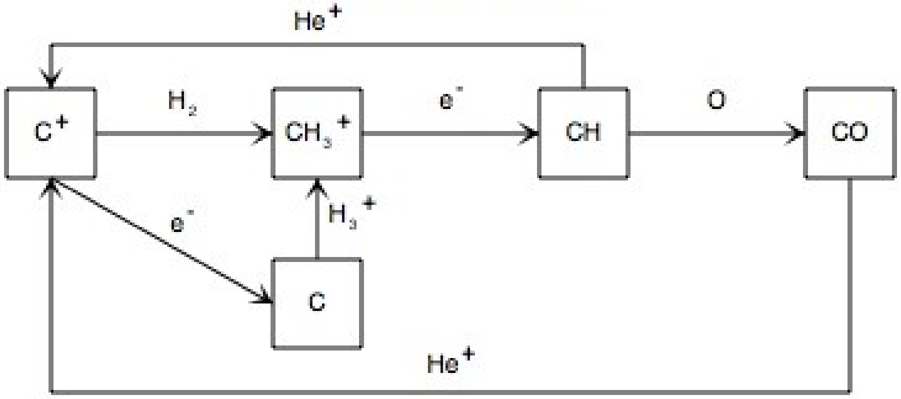
- Need a source of ionization to power chemistry at low temperatures.
- In ISM cosmic rays provide consistent ionizing flux
- In disks (to be discussed later):
  - Cosmic rays (maybe)
  - X-rays (on surface)
  - UV (on surface)
  - Radionuclides (everywhere but at a lower level)

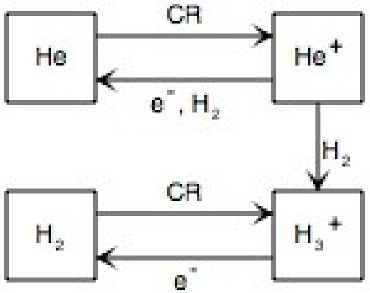
Carbon - Oxygen Chemical Network

Oxygen Chemistry



Carbon Chemistry





Example of H_3^+

Formation:

$$\zeta + H_2 \rightarrow H_2^+ + H$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

Ionization is the rate limiting step so can skip the intermediate reaction (for this example!)

$$\zeta + H_2 \rightarrow H_3^+ + H$$

Destruction:

$$H_3^+ + CO, N_2, H_2O \rightarrow HCO^+, N_2H^+, H_3O^+$$
$$H_3^+ + e^- \rightarrow H_2 + H$$

Example of H_3^+

$$\frac{dn(H_3^+)}{dt} = \zeta n(H_2) - [k_1 n(CO) + k_2 n(N_2) + k_3 n(H_2O) + n_e \beta] n(H_3+)$$

Make a system of equations like this and use a STIFF ODE solver. See Nejad (2005) for a nice discussion.

In equilibrium:

$$\frac{dn(H_3^+)}{dt} = 0 = \zeta n(H_2) - [k_1 n(CO) + k_2 n(N_2) + k_3 n(H_2O) + n_e \beta] n(H_3+)$$

$$n(H_3^+) = \frac{\zeta n(H_2)}{k_1 n(CO) + k_2 n(N_2) + k_3 n(H_2O) + n_e \beta}$$

$$x(H_3^+) = \frac{\zeta}{[k_1 x(CO) + k_2 x(N_2) + k_3 x(H_2O) + x_e \beta] n(H_2)}$$

Gas–Grain Interaction

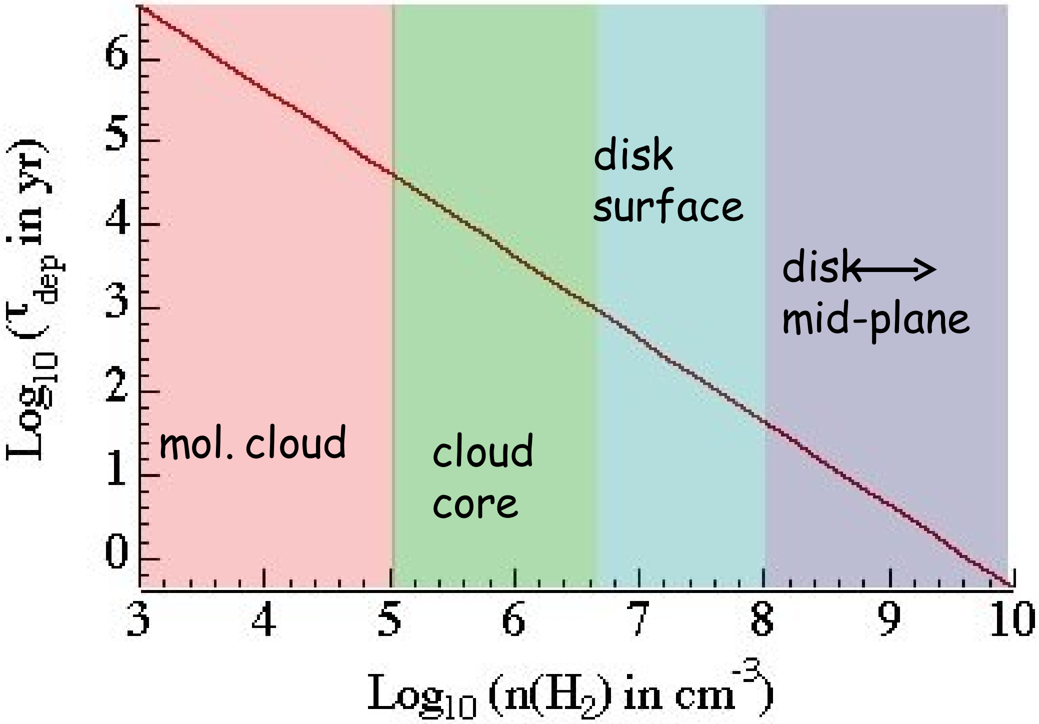
- Freeze–out
- Thermal Desorption (Sublimation)
  - Binding energy to surface
- Non–Thermal Desorption
  - Photodesorption
  - X–ray
  - Cosmic Ray
- References:
  - Tielens ISM Book
  - Tielens and Allamandola 1987 – Interstellar Processes
  - Watson 1972 Rev. Mod. Phys.
  - Leger, Jura, and Omont 1985; d'Hendecourt et al. 1985

Theory: Gas Phase Freeze–out

- depletion timescale (collision time for molecule with grain surface):

$$\tau_{dep} = \frac{1}{\sigma_{gr} v S n_{gr}}$$

$$\tau_{dep} \approx \frac{4 \times 10^{9}}{S n_{H_2}} yr$$



- Sticking coefficient: generally assumed to be unity.
  - —Likely the case for heavy molecules
  - —Laboratory work is consistent with this (Bisschop et al. 2006)
- $\sigma_{gr} = \pi a^2$ with a = grain radius
- Clearly there is a (variable) size distribution of grains – desorption mechanisms capable of clearing small grains – take 1000 Å as fiducial size

Binding Strength

- Chemical adsorption: chemisorption
  - chemical bonding between particle and surface.
  - $E_b \sim 0.5 - 5$ eV (> 6000 K)
  - not expected to occur under interstellar conditions (have to break a bond to make one)
- Physical adsorption: physisorption
  - van der Waals interaction between particle and surface.
  - $E_b \sim 0.1 - 0.3$ eV ($1000 - 2000$ K)
  - strength proportional to the polarizabilities of both surface and approaching particle.
  - Will also depend on surface – which likely has a distribution of sites with a range of E_b

Recent measurements of E_b for relevant ices summarized in Collings and McCoustra (2005) IAU 231, Astrochemistry

$E_b(CO{-}CO) = 830$ K; $E_b(H_2O{-}H_2O) = 5800$ K

Theory: Gas Phase Freeze-out

Thermal Evaporation:

$$\tau_{evap} = \nu_0^{-1} e^{-E_b/kT_d} \ s^{-1}$$

$$\nu_0 = vibration frequency = \sqrt{\frac{2N_s k E_b}{\pi^2 m}}$$

N_s is the surface density of sites $\sim 1.5 \times 10^{15}$ cm^{-2} and m is the molecular mass

$\nu_0 \sim 10^{12}$ s^{-1}

Theory: Gas Phase Freeze–out

Thermal Evaporation:

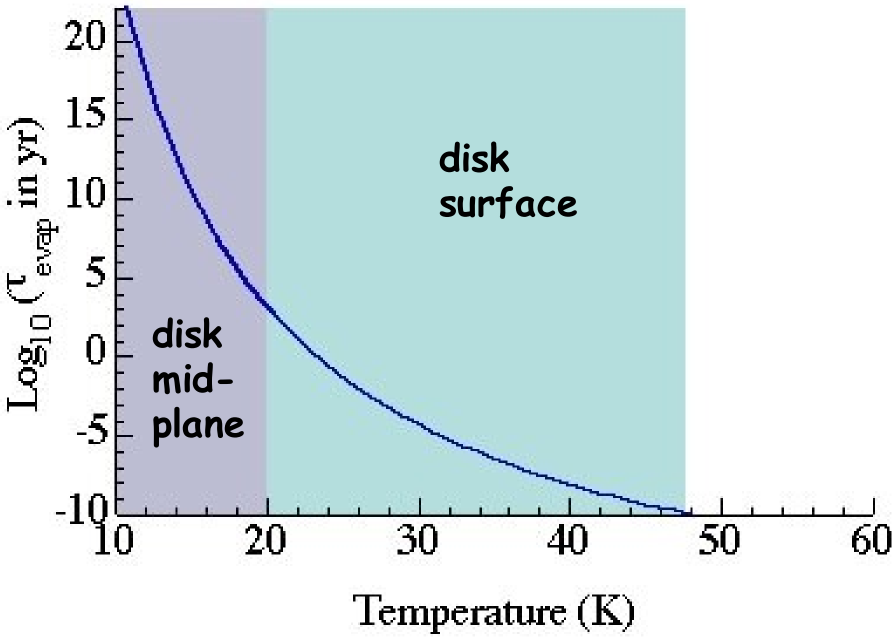
$E_b(CO - CO) \sim 830$ K
$E_b(CO - H_2O) \sim 1180$ K
$E_b(N_2) \sim E_b(CO)$
$E_b(H_2O - H_2O) = 5600$ K

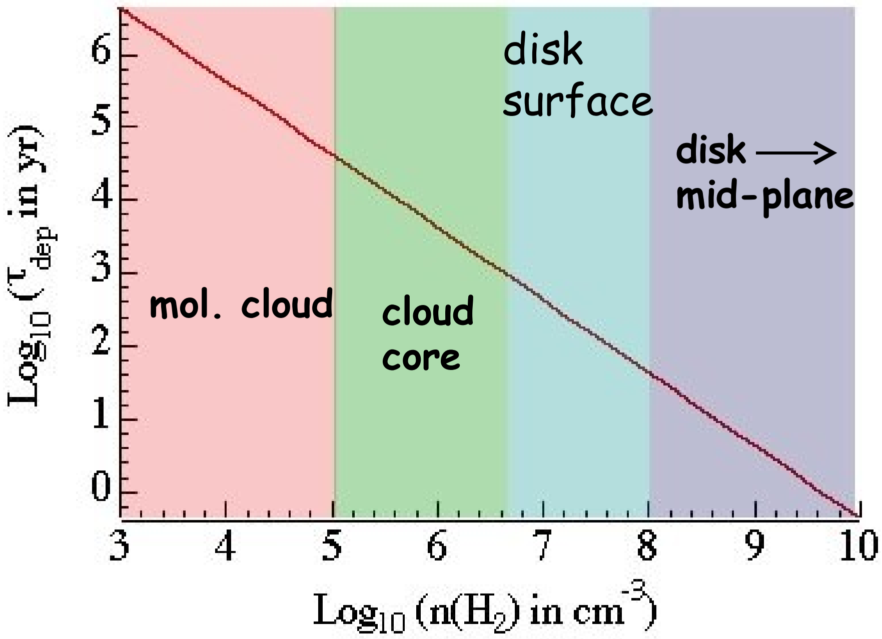
E_b references:
Collings et al. (2004); Oberg et al. (2005); Fraser et al. (2002)

Modelers use values from Hasegawa et al. (1992)

Also some ices are trapped in water matrix – see Viti et al. (2004) for applications - not been accounted for in disk work.

Theory: Gas Phase Freeze-out



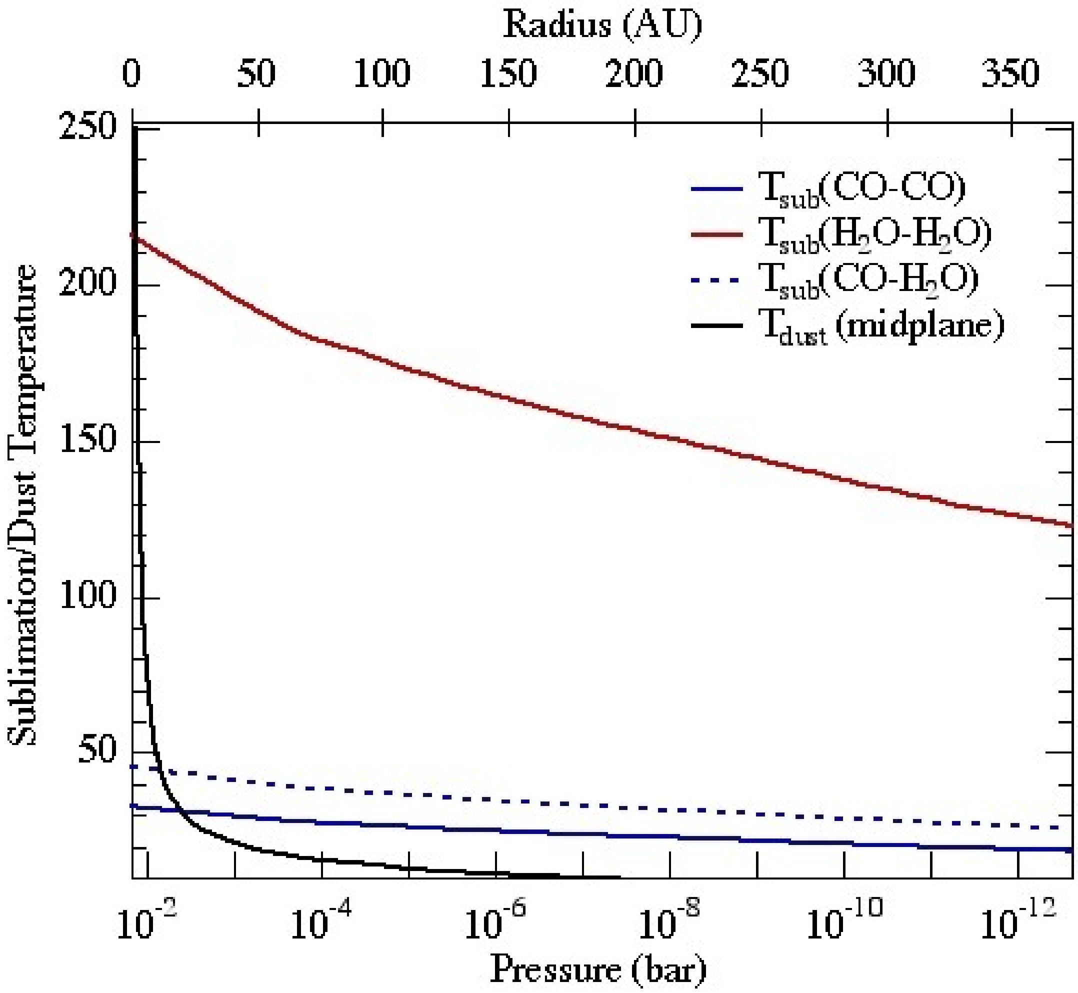


∴ Freeze-out will dominate the disk midplane and a good fraction of the upper layers.

Sublimation Temperature

$$n_{gr}\sigma v = \nu_0 e^{-E_b/T_{sub}}$$

$$T_{sub} = \frac{-E}{ln\left(\frac{n_{gr}\sigma v}{\nu_0}\right)}$$



Photodesorption

Rate of photodesorption (s^{-1}):

$$k_{pd} = G_0 \left(\frac{10^8}{photons\ cm^{-2}\ s^{-1}} \right) \gamma \sigma_{gr} Y e^{-2A_v}$$

γ = fraction of grain covered = $n_x/(n_{gr} N_{site})$

$N_{site} = 4\pi a^2/(2.6\ \text{Å})^2$

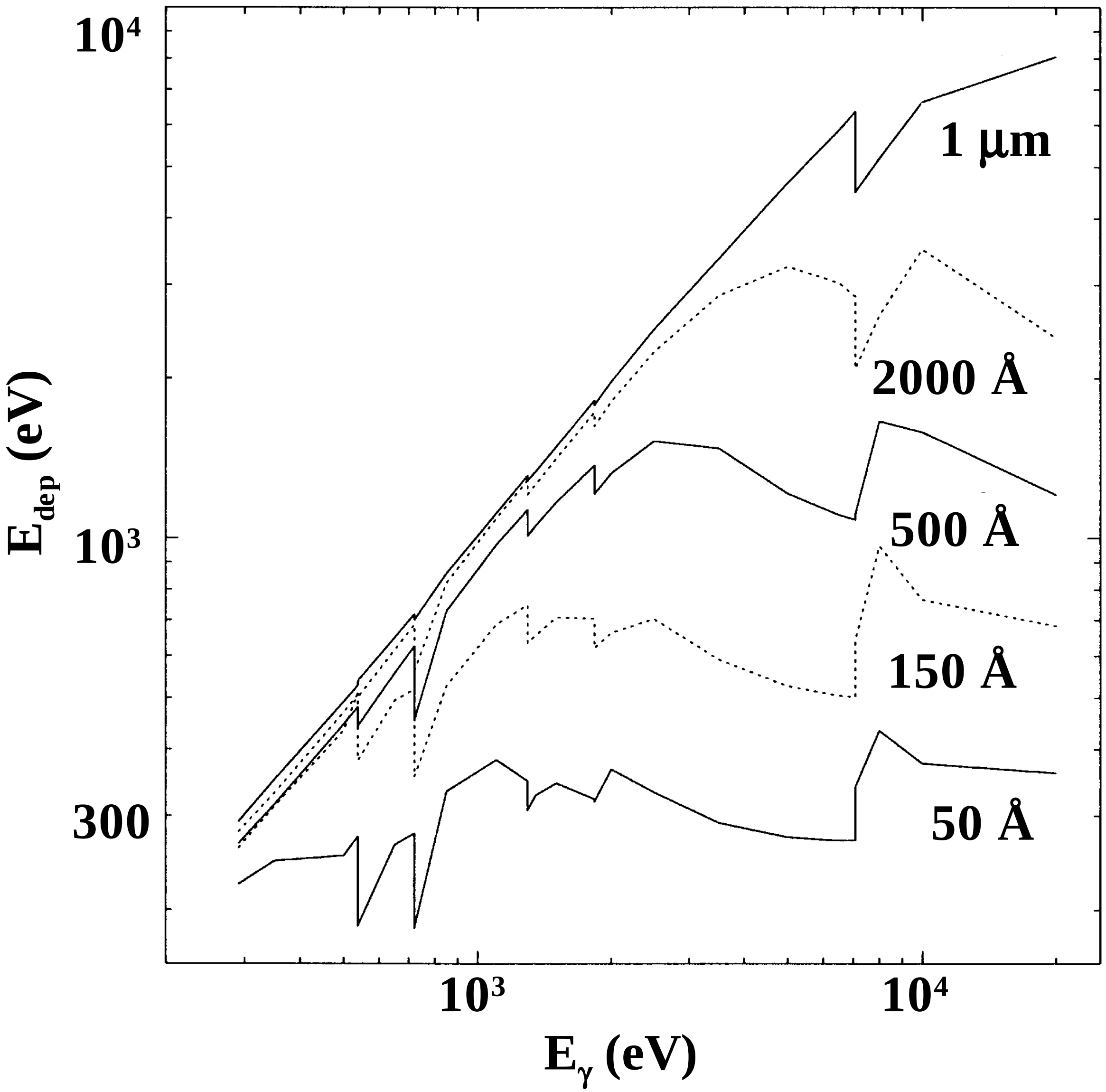
Y = photodesorption yield

$Y(CO) < 10^{-5}$: van Broekhuizen (PhD Thesis), but used Ly α lamp

$Y(H_2O) \sim 10^{-3}$; Westley et al. 2005, but had to radiate ice first

– Not very well known. Models tend to adopt 10^{-4}

X-ray Energy Deposition

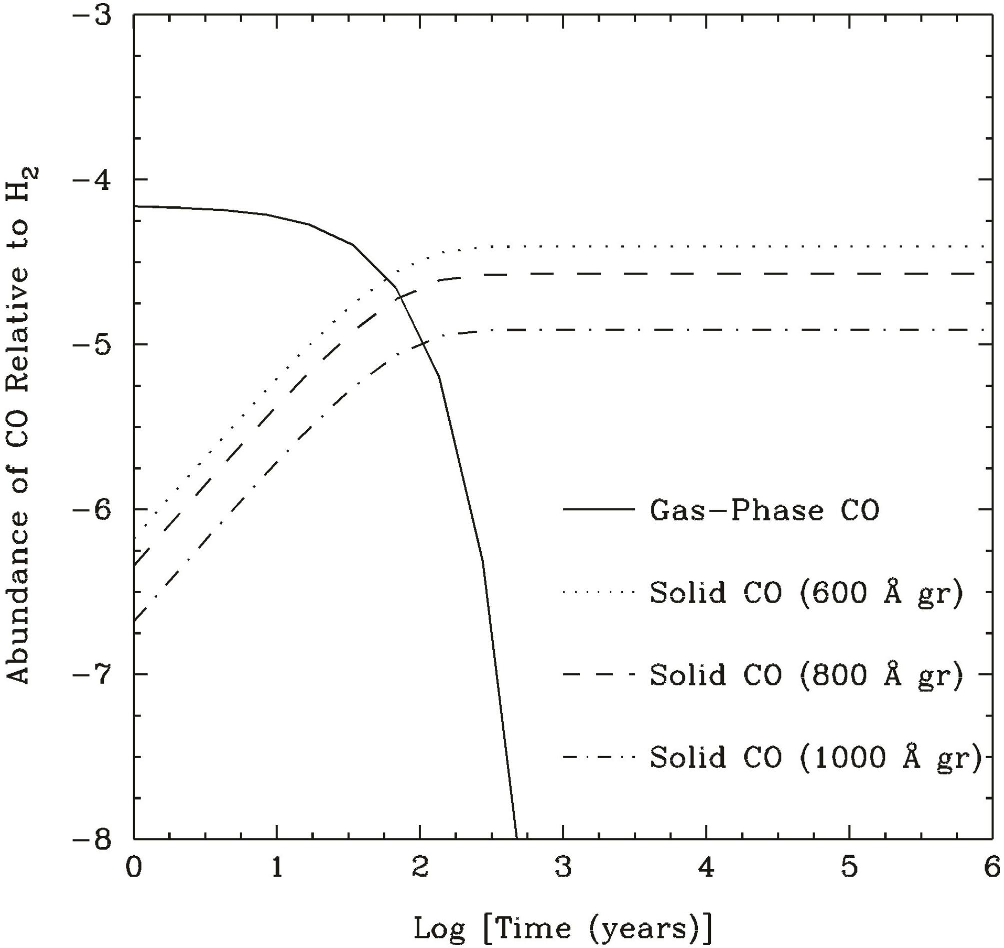


Najita et al. 2001, Using Dwek & Smith 1996

X–ray Whole Grain Heating: MRN Size Distribution

Leger, Jura, and Omont 1985

$$\Delta E(eV) = 3.4 \times 10^{4} \left(\frac{a}{0.1\mu m}\right)^{3} \left(\frac{T_f}{30K}\right)^{3} \quad (for\ T_f < 50\ K)$$



- Najita, Bergin, and Ullom 2001
  - 0.5 – 5 keV photons will heat small grains, a < 150 Å, to T > 50 K.
  - 1 – 4.5 keV photons will heat 300 Å grains to T > 30 K.
  - a > 500 Å grains thermalize to T < 25 K.

X-ray Spot Heating

- Solve spatial and time-dependent heat transfer throughout aggregate by solving heat transfer equation:

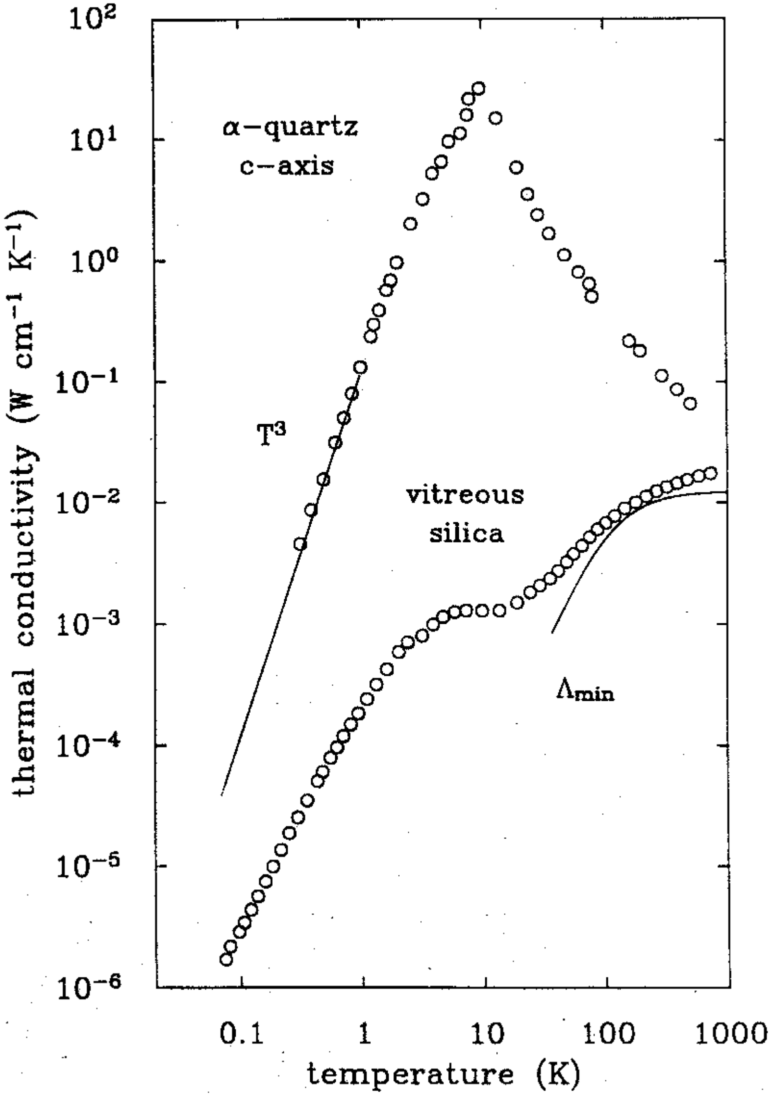
$C_V(T)$ = specific heat at constant volume

$\kappa(T)$ = thermal conductivity

A_{eff} = effective connecting area = πr_c^2

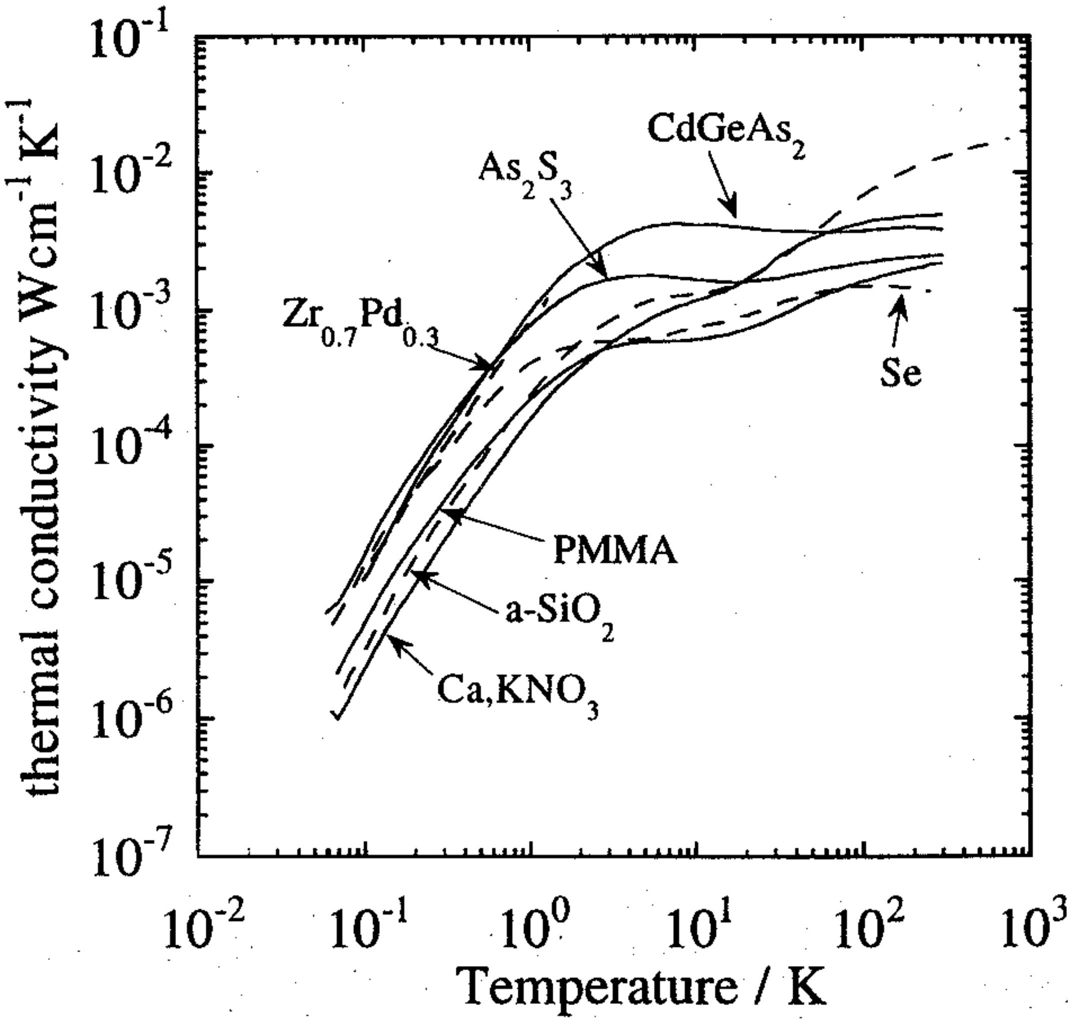
r_c = contact radius

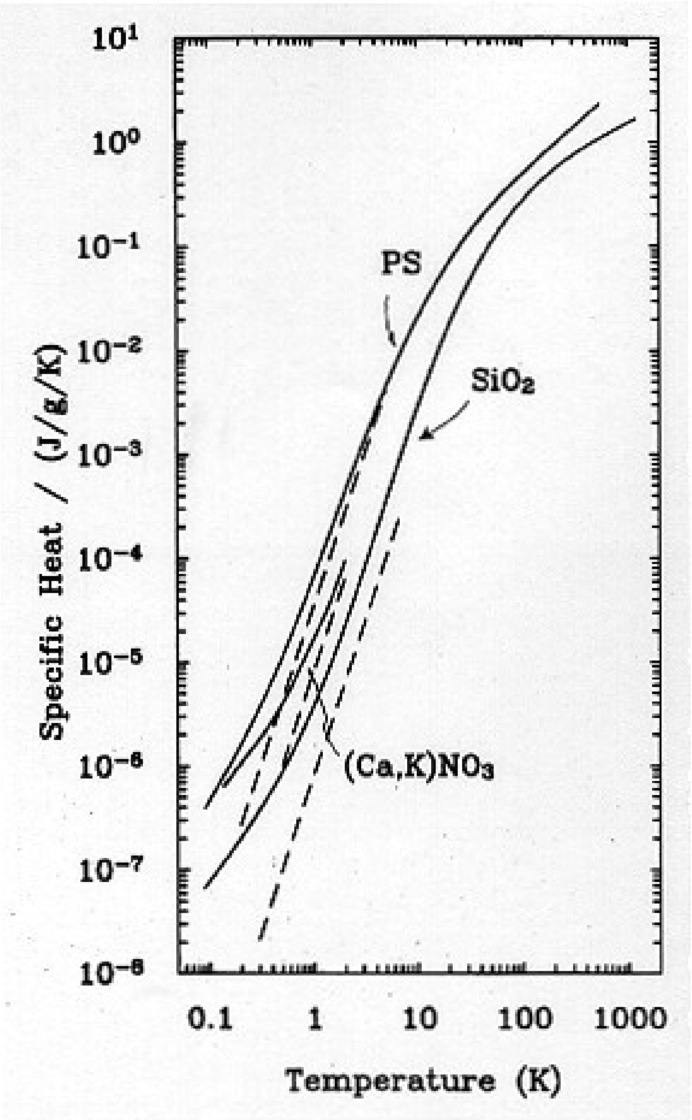
Amorphous Silica Thermal Conductivity



Zeller and Pohl 1971

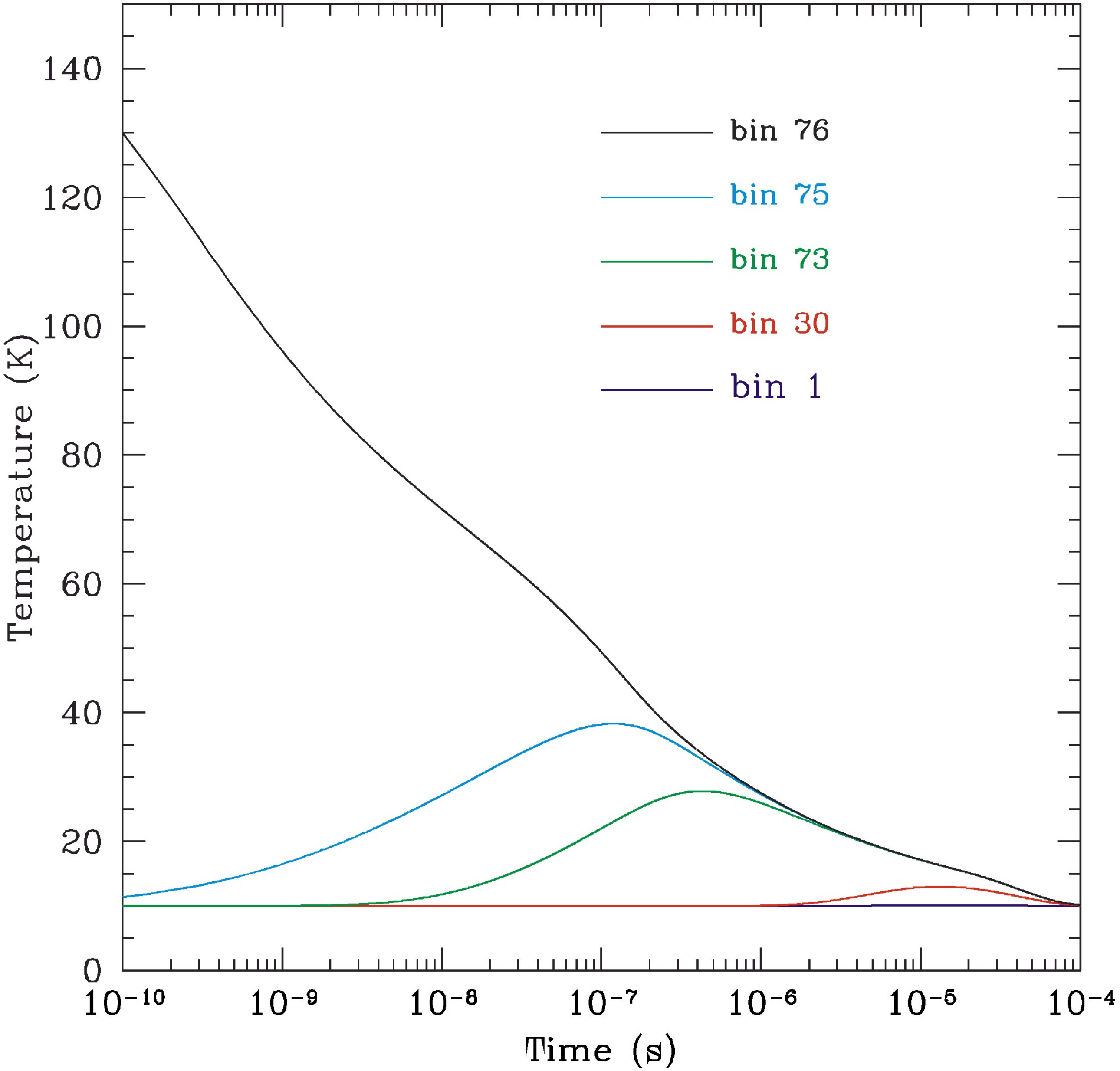
Amorphous Solids: "Universal" Thermal Conductivity and Specific Heat



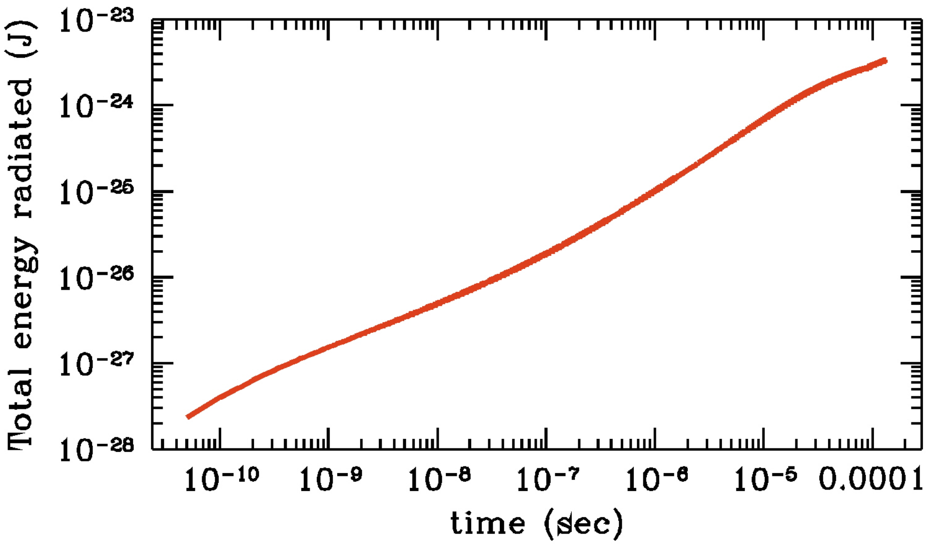


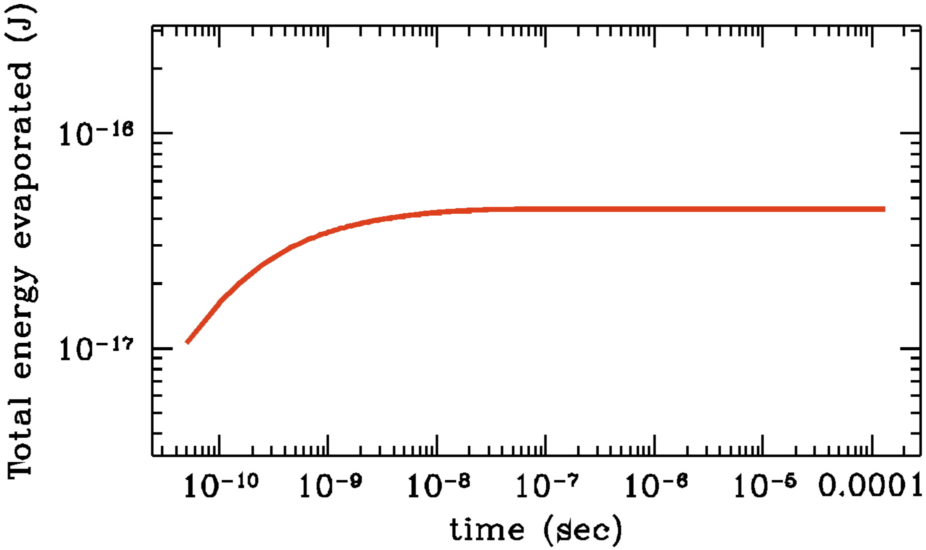
Pohl 1998

X-ray Spot Heating: Heat Diffusion



X-ray Spot Heating: Energy Losses





Capable of enhancing abundances of volatiles (likely not H_2O)
Commercially usable rates not currently available.

Najita et al. 2001

Cosmic Ray Desorption

- Cosmic rays have energies between 0.02 and 4 GeV per nucleon and could potentially penetrate deep into disks.
- Protons are more abundant than heavier atoms but energy deposition goes as Z^2 (Leger et al.

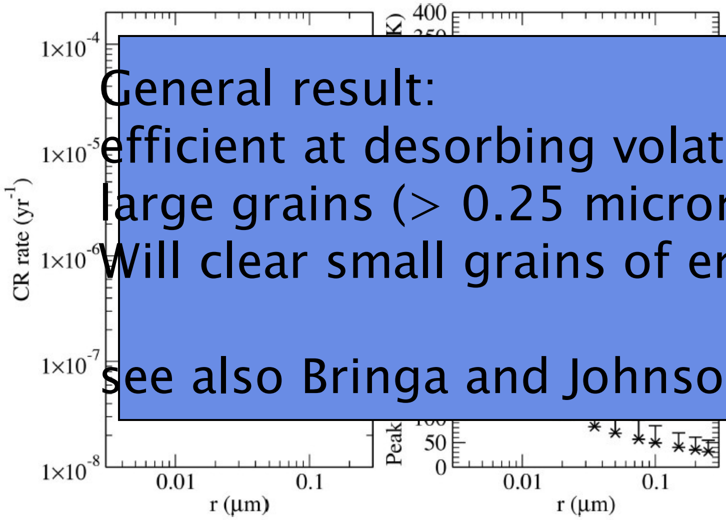


Fig. 2. The results of interactions between grains and cosmic rays. (*Left*) The cosmic ray collision rate for Fe nuclei as a function of the granular radius. (*Right*) The distribution of peak temperatures after cosmic-ray bombardment vs. granular radius with the mode depicted by a cross. Olivine grains are shown in *Upper*, and carbonaceous grains are shown in *Lower*. The bars indicate the temperatures for which 99% of the determinations fall.

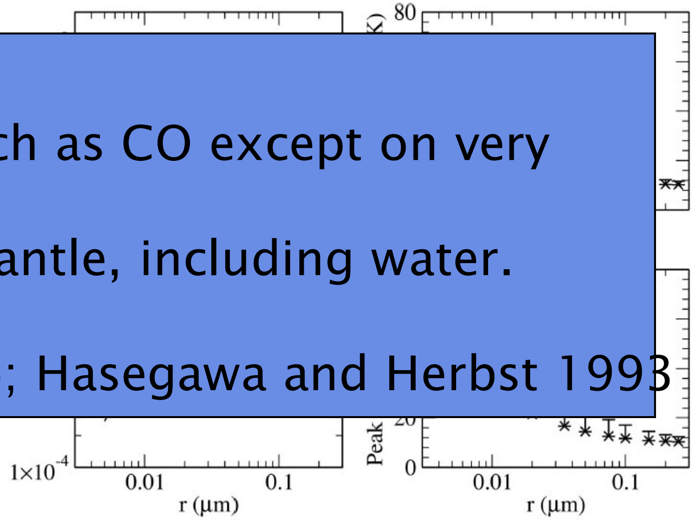


Fig. 3. As in Fig. 2, but for protons.

General result:
efficient at desorbing volatiles such as CO except on very large grains (> 0.25 microns)
Will clear small grains of entire mantle, including water.

see also Bringa and Johnson 2004; Hasegawa and Herbst 1993

Herbst and Cuppen 2006 (PNAS)

Explosive Desorption

- Experiments of irradiated ices in the lab suggest that when mantle is warmed to ~ 25 K then the rapid movement and reactions of radicals leads to an explosion of chemical energy.
  - could lead to explosive desorption of the mantle (Schutte and Greenberg 1991)
  - issues: needs radicals -- likely present on surface, but midplane would need mixing?
- Grain-grain collisions could potentially reach this temperature in disks (Willacy et al. 1998)
  - collision timescale is ~ 2×10^{14} yrs/n_H
  - less than depletion timescale

Grain Surface Chemistry

- for summary: Herbst et al. 2005, J. Phys. Conf. Ser. 6, 18
  - classic refs: Hollenbach and Salpeter 1972; Tielens and Hagen 1982; Hasegawa et al. 1992
  - New work: Biham (2005, IAU), Stantcheva et al. 2002
- Responsible for creation of H_2
- At low temperatures (< 20 K) H atom addition will dominate -- only H (and to a lesser extent D) can scan the surface – likely leads to saturated molecules.
- At higher temperatures heavier atoms (radicals?) can potentially move around -- will make complex species.
- For disks 3 key points:
  - $x(H) \propto 1/n$ so may fall below 1 H atom per grain
  - are warm regions that can activate heavier atoms/molecules on surface
  - ???????