



An Introduction to Astrochemical Modelling

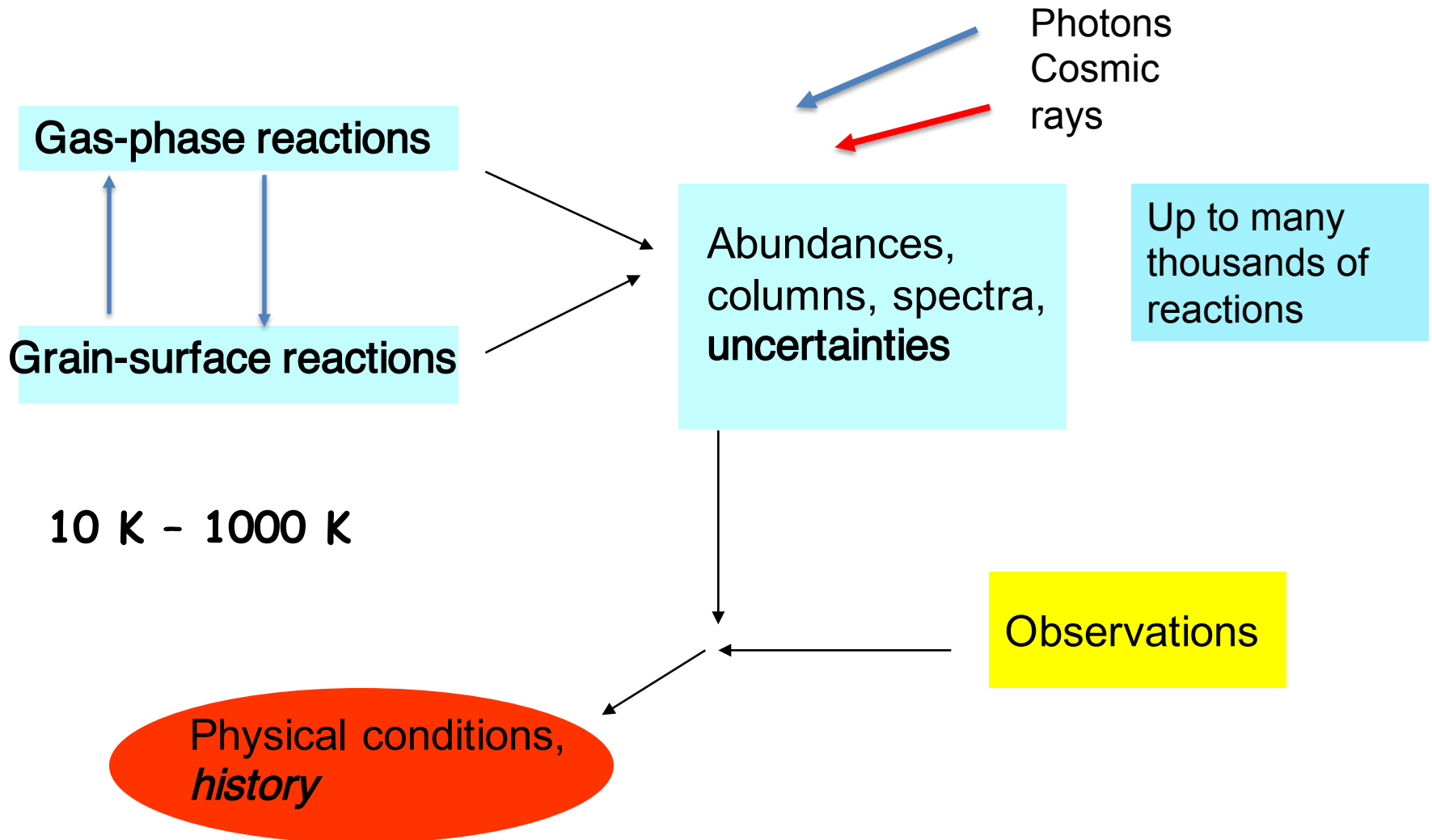
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Why develop chemical models?

- Chemical models represent an attempt to understand the chemistry occurring in assorted sources and use this understanding to:
 - 1. help determine the physical conditions of the source as well as its age,
 - 2. improve our knowledge of exotic chemical processes
 - 3. predict how large molecules can grow.

Chemical Models



Some Model Parameters

- Temperature (gas and grain can be different)
- Density
- Visual extinction (optical depth)
- Elemental abundances in gas/mantle
- Grain size or size distribution
- Gas-to-dust ratio
- Accretion fraction
- Initial abundances of molecules

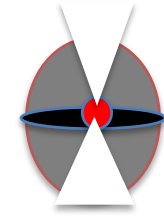
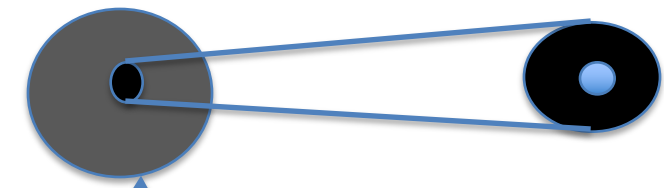
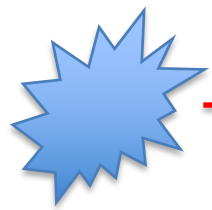
Cold Core; 10 K;
 10^4 cm^{-3} exotic
chemistry

Pre-stellar
core; 10 K

Protostar &
hot corino
(100 K)

Protoplanetary
disk; solar
system

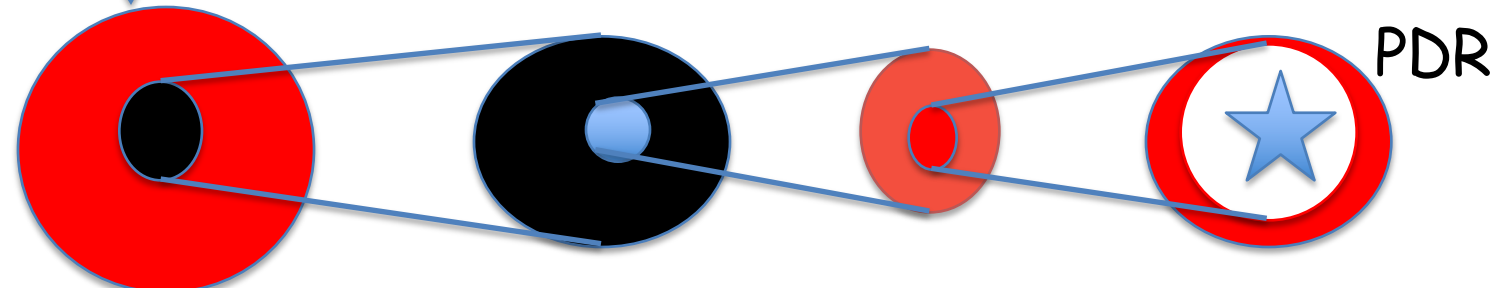
Low mass



Terrestrial organics
(COMs)

CURRENT STATUS

High mass



Infrared dark
cloud
10 - 20 K

HMPO
20-80 K

Hot Core
100-300 K

Bright star;
HII region

Terrestrial organics

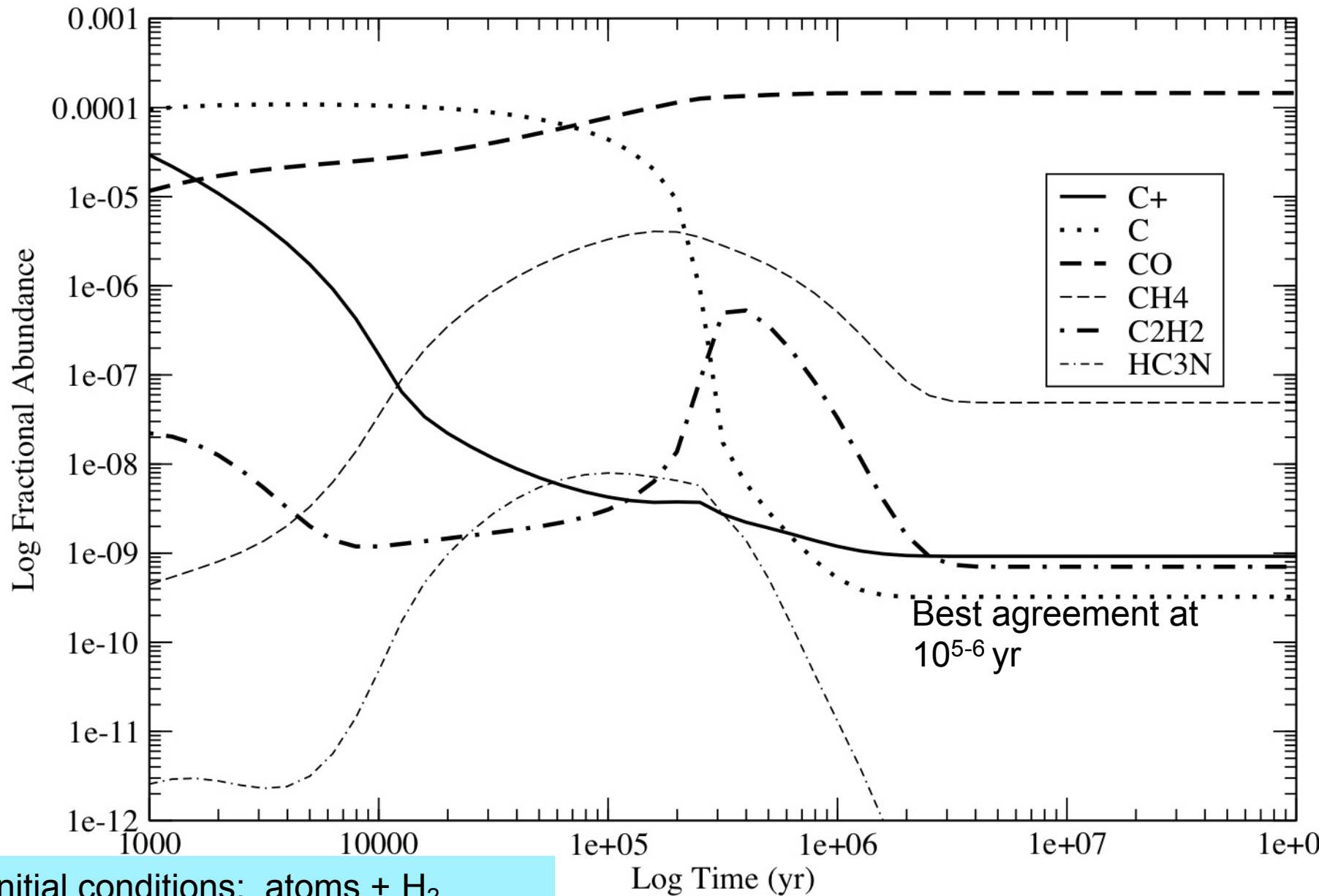
Methods of Solution of Chemical Abundances

- Solution of stiff sets of kinetic differential equations involving both gaseous and dust particle species, coupled by adsorption and desorption. $dn_i/dt = \text{formation} - \text{destruction}$
- Stochastic (probabilistic) and Monte Carlo approaches, especially for small numbers of reactive species on dust particles; e.g. less than one.
- Modified equations to take into account some aspects of stochastic models.

Types of Models (Basic)

- **Cold cores:** Homogeneous (0-D) but pseudo-time-dependent
- **Photon-dominated regions** heterogeneous (1-D) steady-state
- **Hot cores:** homogeneous but time-dependent (warm-up)
- **Protoplanetary disks:** Heterogeneous (2-D) but pseudo-time-dependent

GAS PHASE PSEUDO-TIME-DEPENDENT MODEL OF COLD CORE



Initial conditions: atoms + H₂

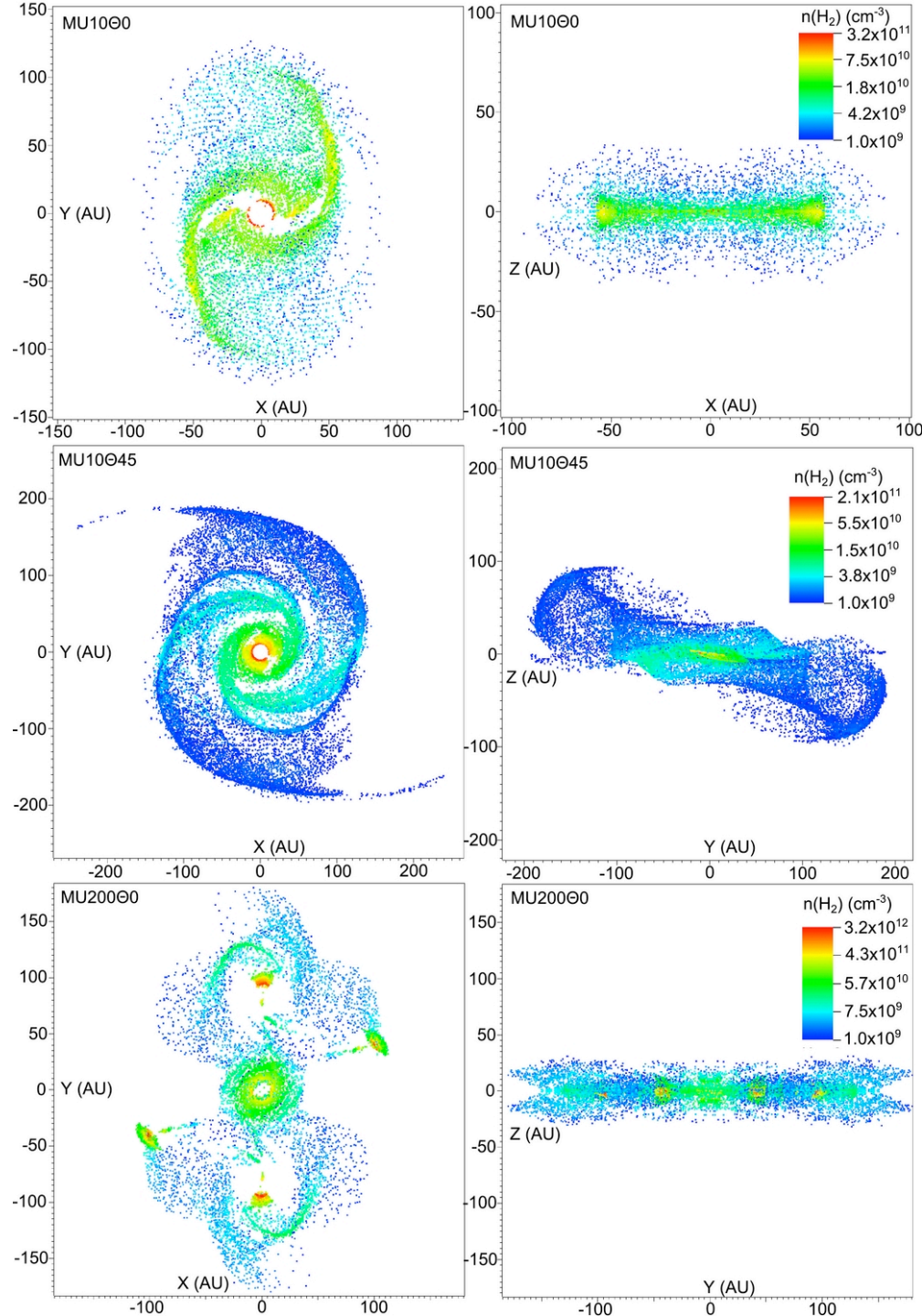
General Problems for Chemical Simulations

- 1. Heterogeneous and/or time-dependent physical conditions, possibly requiring three-dimensional magneto-hydrodynamics.
- 2. Uncertain role of shocks and turbulence.
- 3. New high spatial resolution studies (e.g. with ALMA, NOEMA) require explanations of differing distributions of similar species.
- 4. **What reactions to include?** Has come about historically. Basic chemistry now in datasets such as KIDA, Nautilus, UDFR, etc. although gas-phase emphasized. Sensitivity analyses recently extended for first time to surface chemistry.

The Role of 3D Hydrodynamics

A young protoplanetary disk obtained by hydrodynamic code using the trajectory approach.

Hincelin et al. 2013



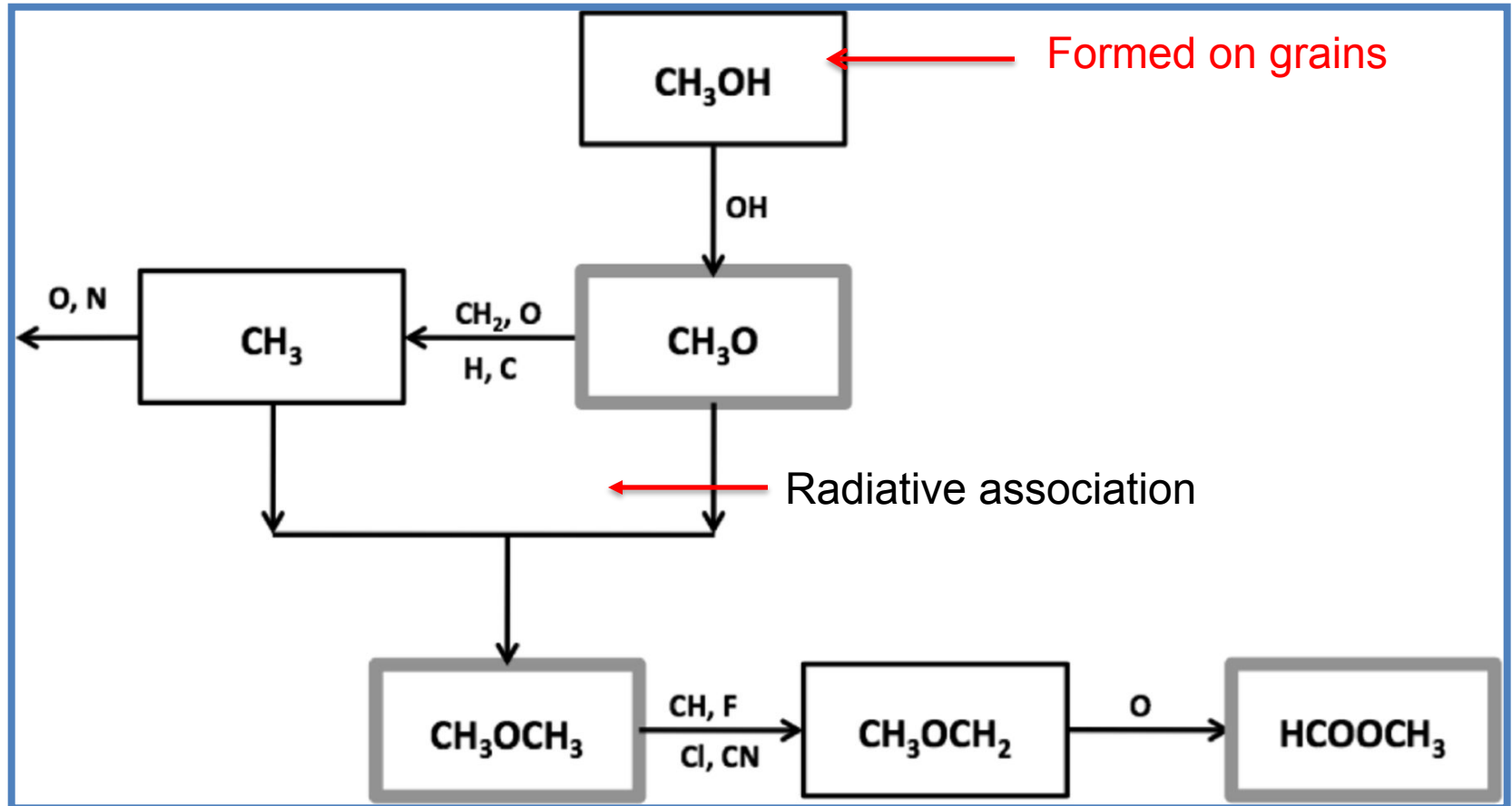
Gas-Phase Reactions

- 1. Ion-neutral: $C^+ + C_2H_2 \rightarrow C_3H^+ + H$
- 2. Dissociative recombination: $H_3O^+ + e \rightarrow OH + 2H$
- 3. Radical-neutral: $CN + C_2H_2 \rightarrow HC_3N + H$
- 4. Radiative association: $CH_3^+ + H_2 \rightarrow CH_5^+ + hu$
-
- As temperature increases, more reactions with barriers and endoergicities need to be included.
- At low temperatures (10 K), tunneling can be important, as in $OH + CH_3OH \rightarrow H_2O + CH_3O$

Some Gas-phase Chemical Problems Remaining

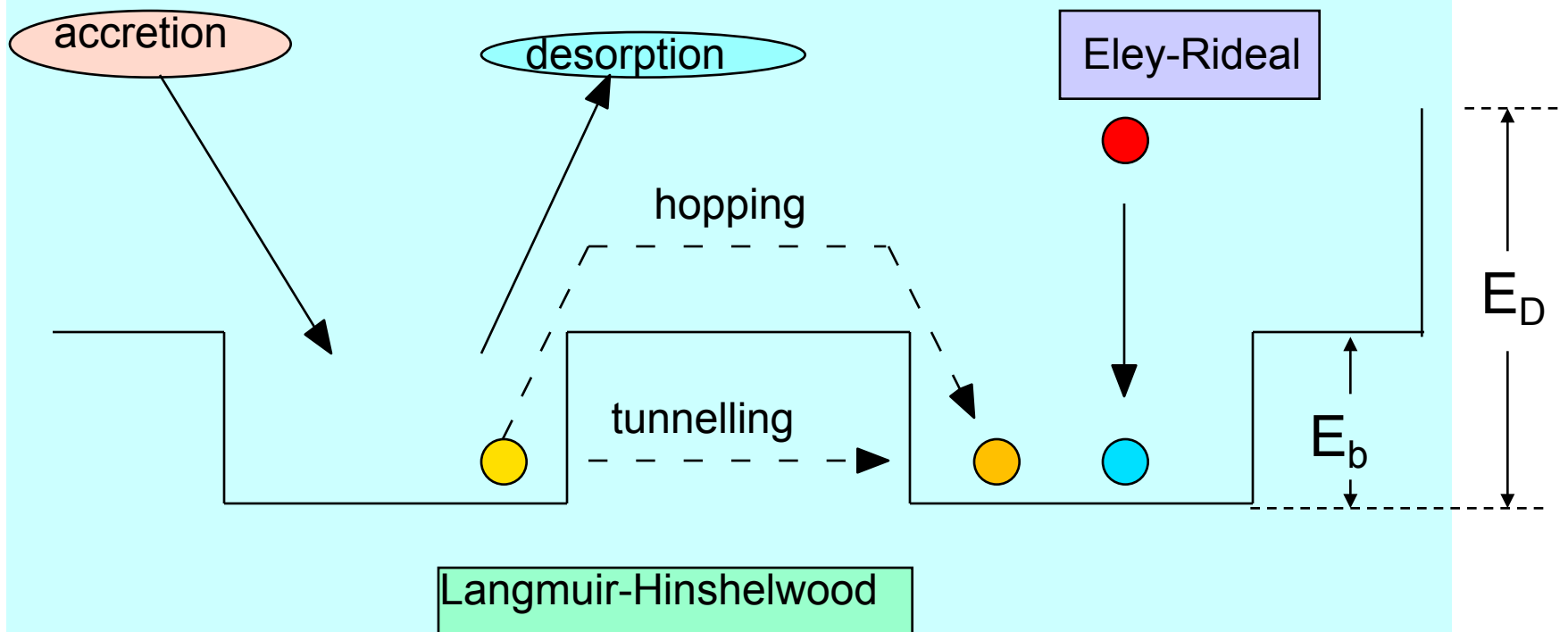
- 1. Low (10 K) and high (1000 K) temperatures not well studied. Extrapolations to low temperature fragile.
- 2. Radiative association and radiative attachment barely studied at all.
- 3. Role of tunneling may be greater than thought.
- 4. Explanation of saturated COMs in cold sources (CH_3OCH_3 ; HCOOCH_3 & isomers); neutral-neutral vs ion-neutral with important role of ammonia.

Neutral-Neutral Synthesis of Dimethyl ether and Methyl Formate



Balucani+ (2015) low temperature neutral-neutral reactions

Two Surface Reactive Mechanisms



Well depths and barriers representative of physisorption.

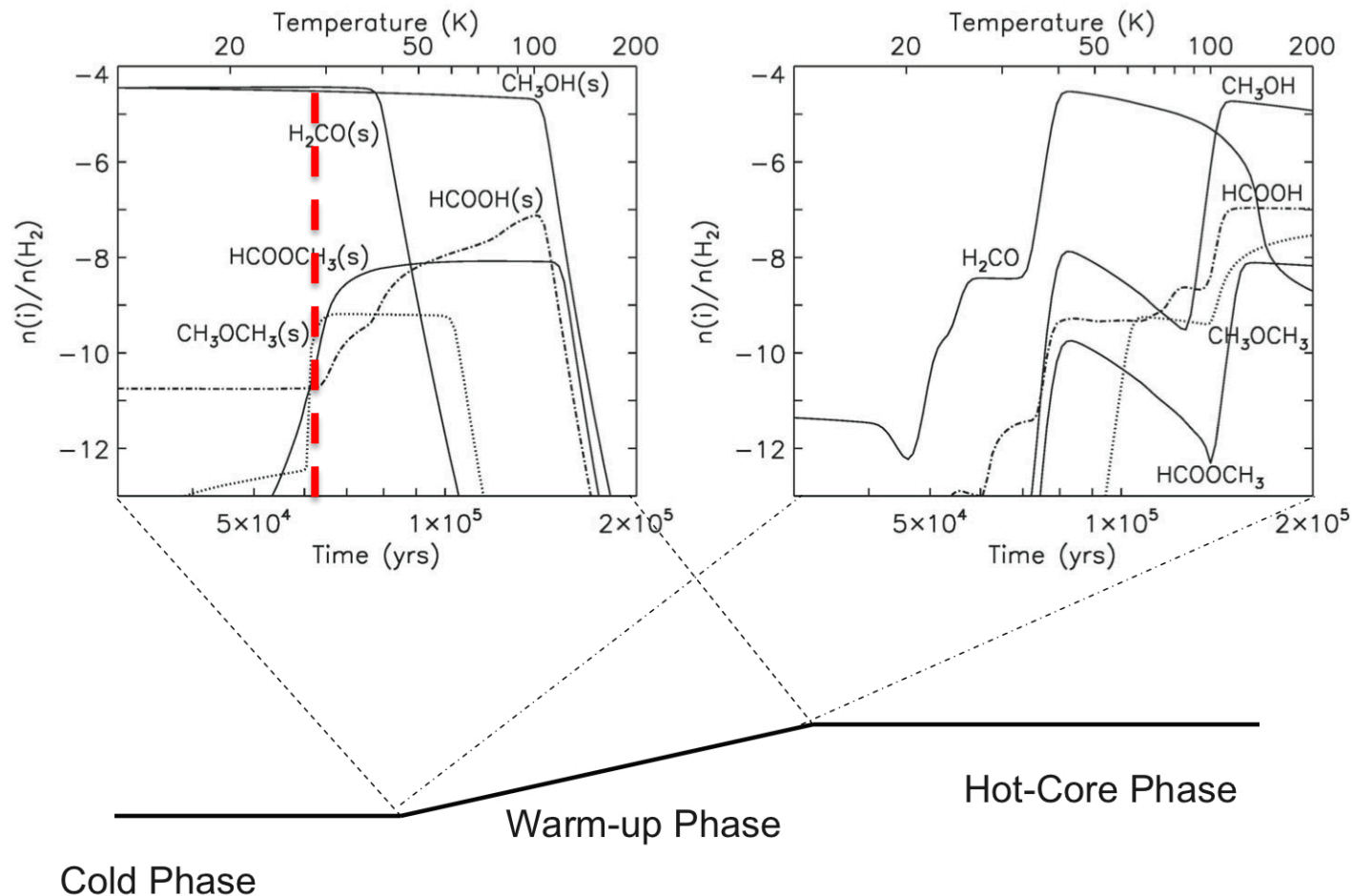
Rate Equation for Diffusive Reaction on Surface

$$\frac{dn_{gr}(A)}{dt} = k_{BC}n_{gr}(B)n_{gr}(C) - k_{AD}n_{gr}(A)n_{gr}(D) - k_{des}n_{gr}(A) + k_{ads}n(A)$$

Surface Diffusive Reactions

- **Low temperature:** atom + molecule ($T < 30$ K)
- e.g. $\text{H} + \text{CO} \rightarrow \text{HCO}$ (despite barrier)
- leads via three subsequent reactions to methanol.
- **Rising temperature:** radical- radical ($T < 100$ K)
- e.g. $\text{HCO} + \text{CH}_3\text{O} \rightarrow \text{HCOOCH}_3$
- (At higher temperatures, thermal desorption occurs. Many such reactions in Garrod et al. (2008) model of hot core chemistry.)
- **High temperatures** (require chemisorption)

Warm-up Models to 200 K (0D)



COMs

From Garrod & Herbst (2006): note that COMs are not produced until 30 K. Radicals formed by photons.

SOME REMAINING GRAIN PROBLEMS

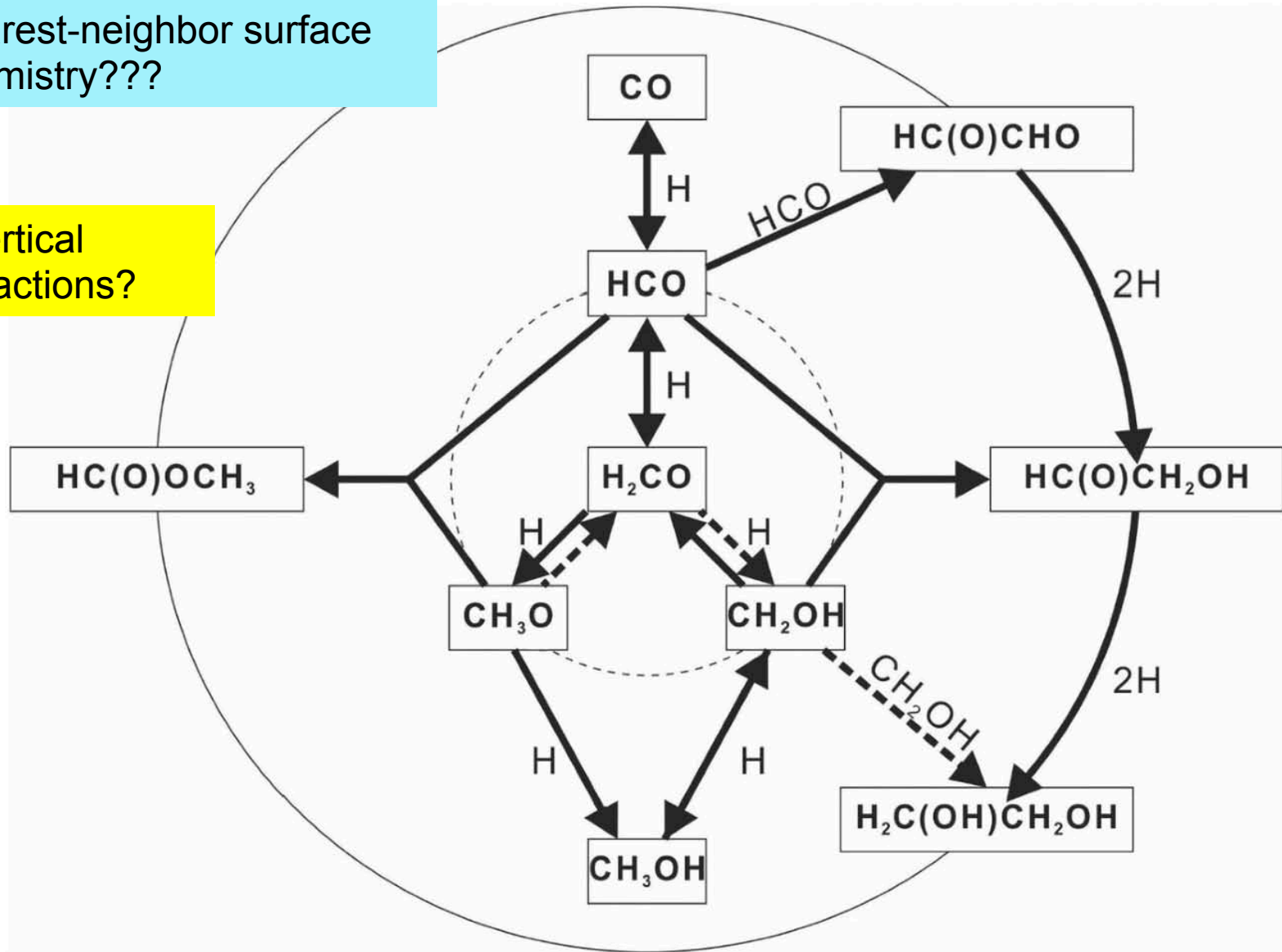
- 1. Relative importance of Eley-Rideal and Langmuir-Hinshelwood mechanisms.
- 2. Radical-radical association (recombination) reactions poorly studied.
- 3. How to treat bulk mantle chemistry in addition to surface chemistry.
- 4. Relation between diffusive barrier and desorption energy. Ratio seems to be becoming more uncertain.
- 5. Role of barriers, including tunneling. Possible competition between diffusive barriers for chemical reactions with their own activation energy.
- 6. Uncertainties in rates of non-thermal desorption at low temperatures (photodesorption, reactive desorption).

Non-thermal Desorption

- **Photodesorption**: a variety of mechanisms with results of desorption per photon rates from 10^{-3} to less than 10^{-5} and competitive role of intact photodesorption vs photodissociation.
- **Reactive desorption**: known to occur, but high uncertainty in results. New result for $\text{H} + \text{O}_3$ on compact water (He et al.) of 11% independent of temperature.

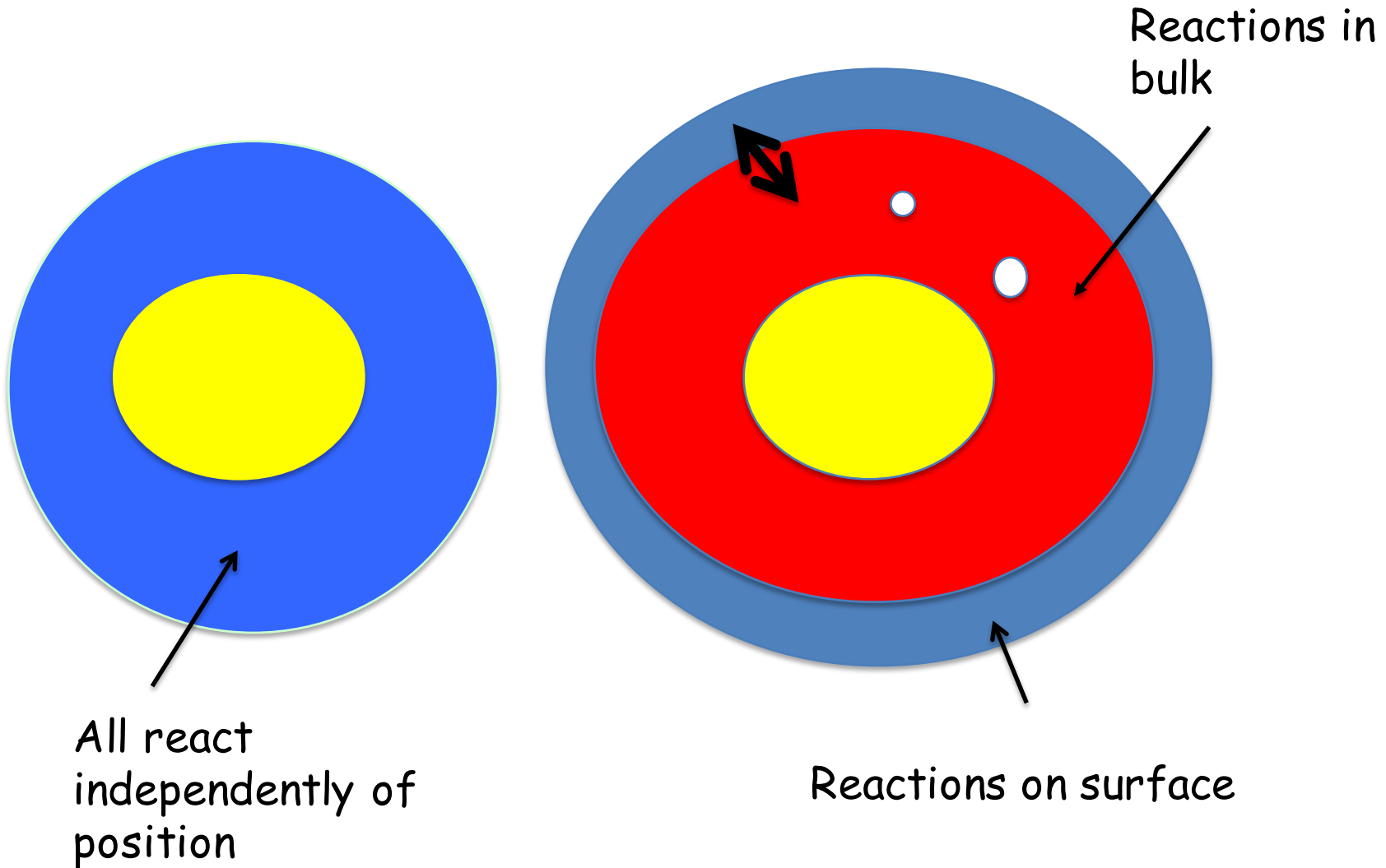
Nearest-neighbor surface chemistry???

Vertical reactions??



Linnartz+2016: atom-radical + radical-radical (T = 10-20 K?)
Thermal conditions; no photons.

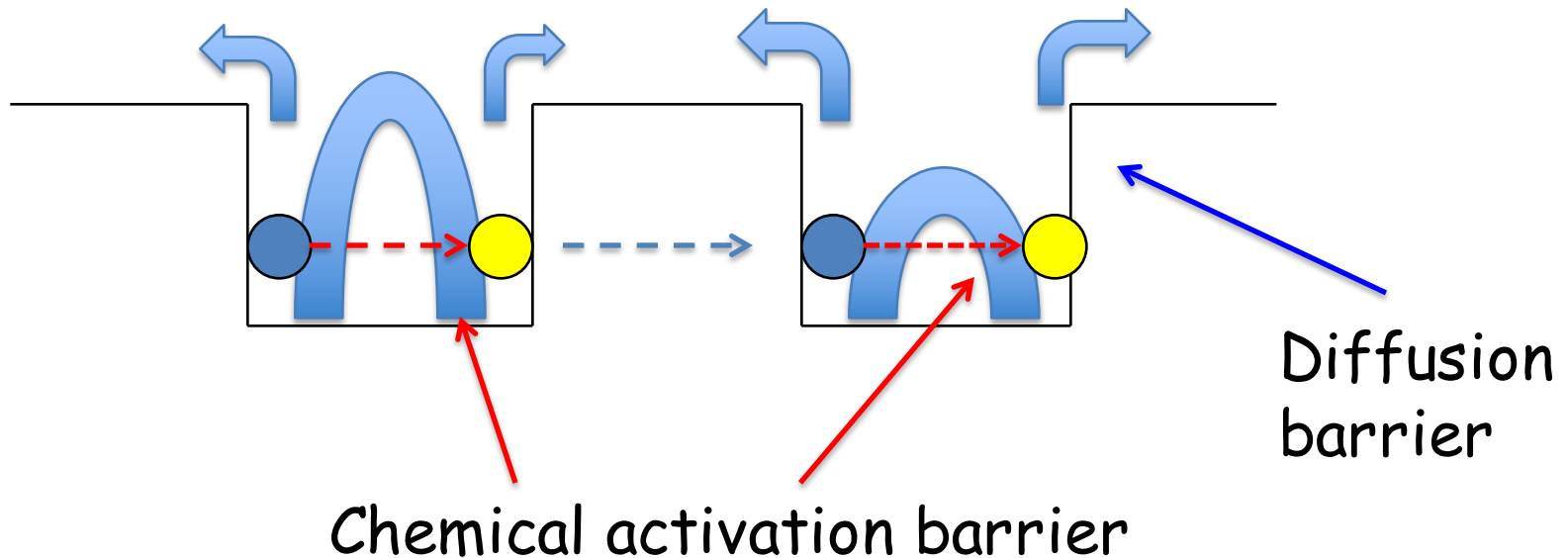
Rate Processes: Two Phase vs. Three Phase



Bulk Mechanisms (Uncertain)

- 1. Inside pores
- 2. substitutional
- 3. interstitial: sites of weak binding.
- 4. Vertical (chain) reactions

Model of Competition



$E_a < E_b$ means that tunneling under the activation energy is more likely than tunneling under the diffusion barrier.

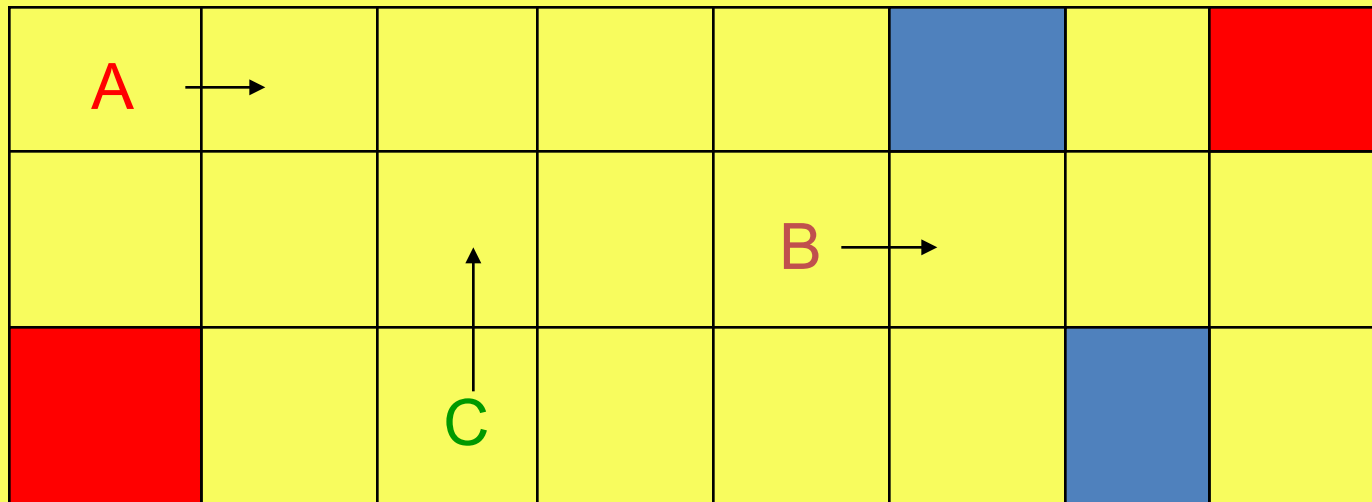
General Problems With Rate Equations

- a) inaccurate treatment of random walk; problem known as “back diffusion”
- b) overestimate of rate in “accretion limit” where average number of reactive particles less than unity and discreteness and fluctuations important (Tielens)
- c) cannot completely take into account microscopic structure of surface (e.g. roughness) and internal ice layers

CTRW (MICROSCOPIC, kMC) APPROACH

Chang, Cuppen & Herbst (2005)

- A Monte Carlo approach in which the actual positions of individual species on a lattice are followed with time. Can use to follow reactions (LH,ER) and mantle build-up.



Problems with MC Approaches

- 1. Must run stochastic approaches for both the grain and gas phases.
- 2. macroscopic-macroscopic most efficient; macroscopic-microscopic least. For latter, can only run about 10^5 yr for cold cores.
- 3. Cannot treat H_2 on/in grains easily.
- 4. Currently, best solutions: Vasyunin, Chang approaches

Accomplishments

- Can reproduce chemistry at least partially in most sources studied and can at times even be predictive.
- Has helped to understand some of the details of stellar evolution.
- Has actually enhanced our knowledge of chemical kinetics, especially at low temperature.

Acknowledgments

- **Sources of Funding:**
- NASA, NSF
- **Recent group members:** Paul Rimmer, Nanase Harada, Donghui Quan, Yezhe Pei, George Hassel, Anton Vasyunin, Tatiana Vasyunina, Qiang Chang, Dawn Graninger, Chris Shingledecker, Ugo Hincelin, Kinsuk Acharyya, Dominique Maffucci, Andrew Burkhardt, Romane Le Gal, Jessica Tennis