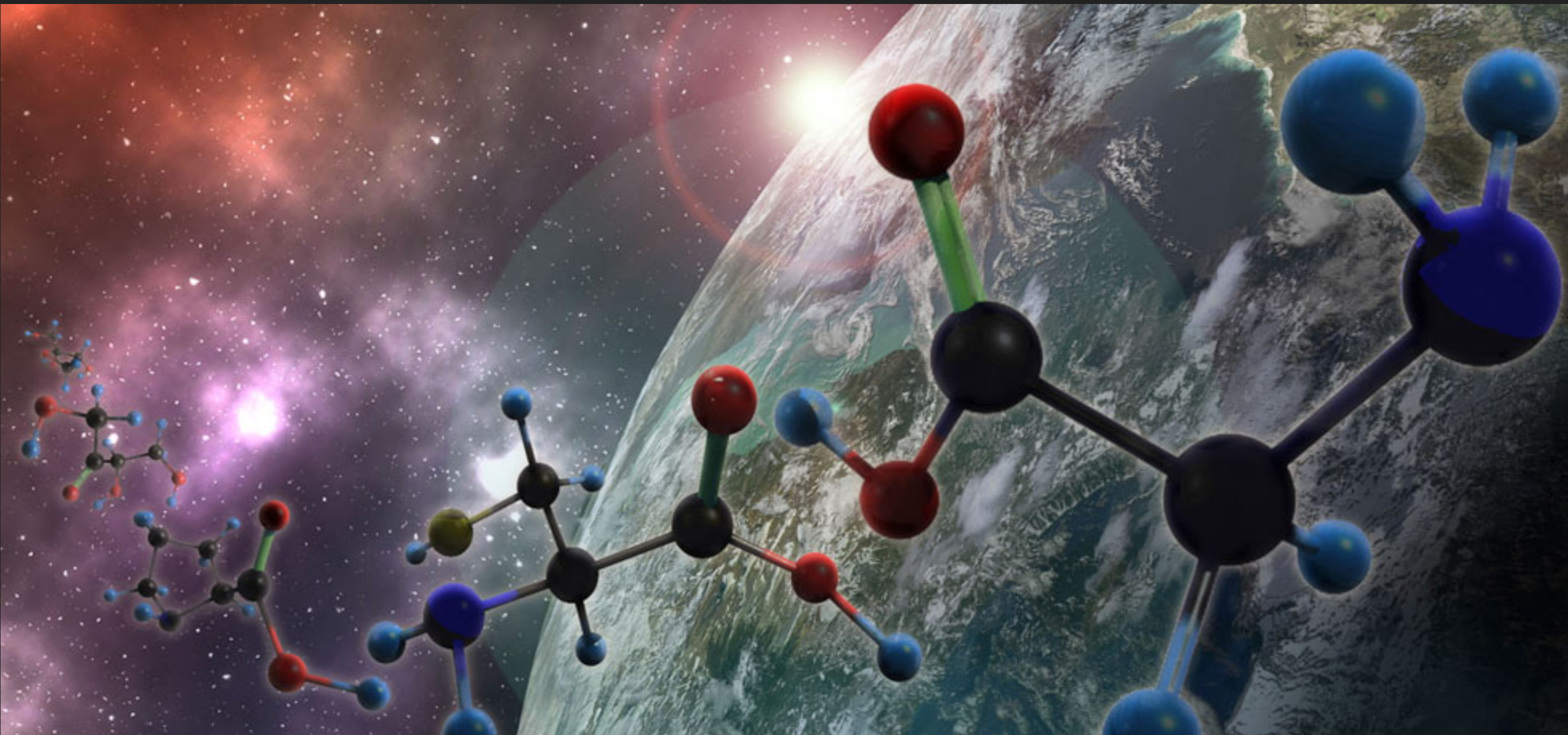


LECTURE 3

STEFANO BOVINO

UNIVERSIDAD DE CONCEPCIÓN



Temperature effect (1)

$$\frac{dn_{\text{P}}}{dt} = k(T)n_{\text{A}}n_{\text{B}} \quad (1) \quad \text{units of } k(T): \text{ cm}^3 \text{ s}^{-1}$$

- The *qualitative* observation is that most reactions go faster as the temperature is raised

Temperature effect (2)

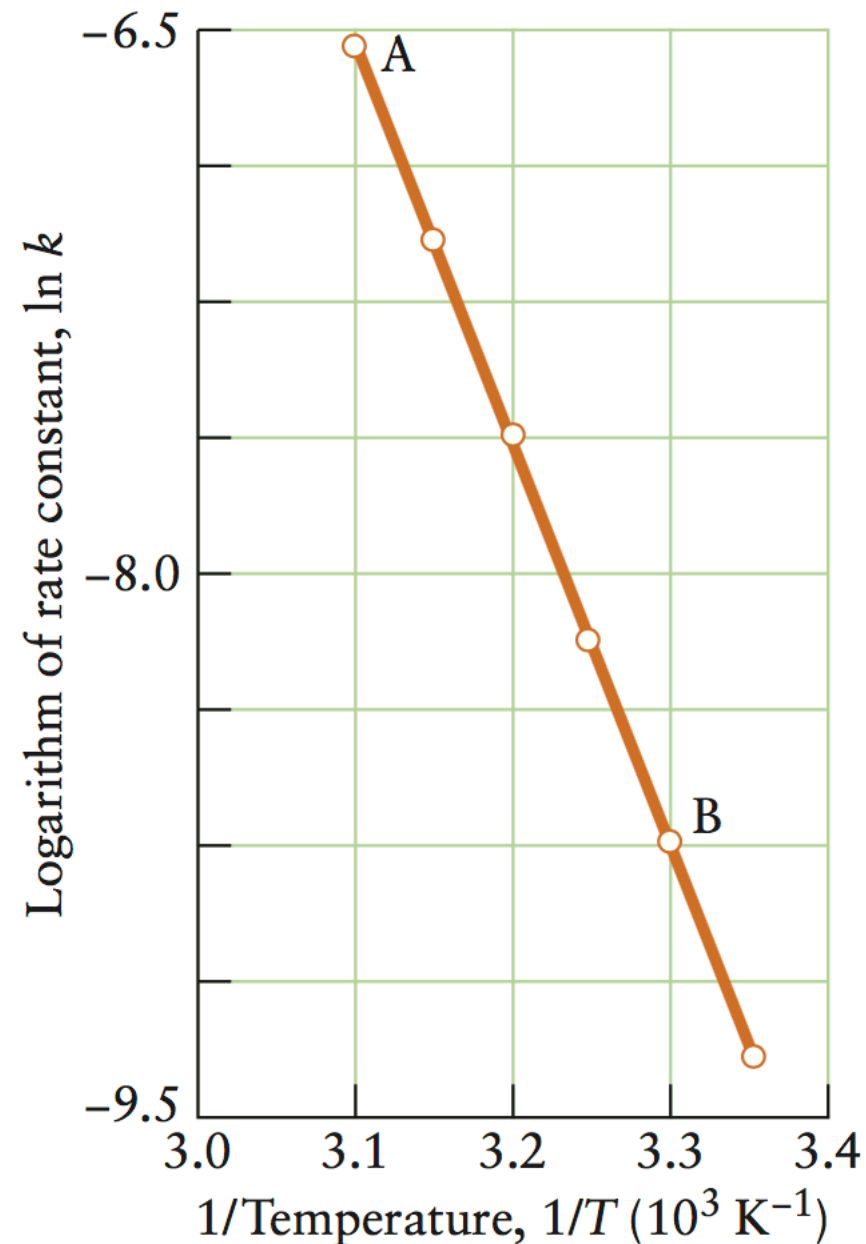
- Swedish chemist Svante Arrhenius found that the plot of the logarithm of the rate constant ($\ln k$) against the inverse of the absolute temperature ($1/T$) is a straight line

$$\ln k = \text{intercept} + \text{slope} \times \frac{1}{T}$$

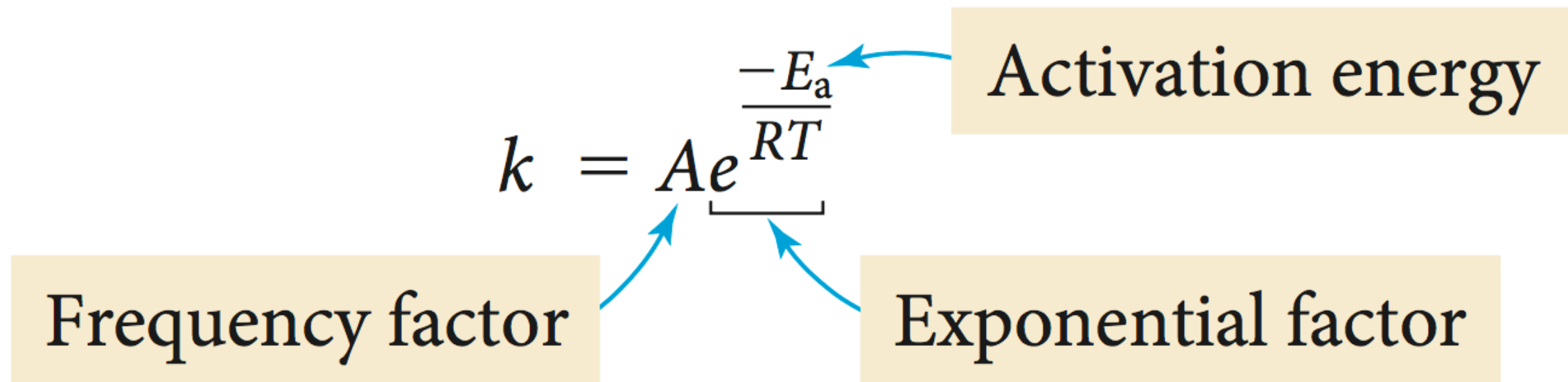
$$\ln k = \ln A - \frac{E_a}{RT}$$

Arrhenius-like rates

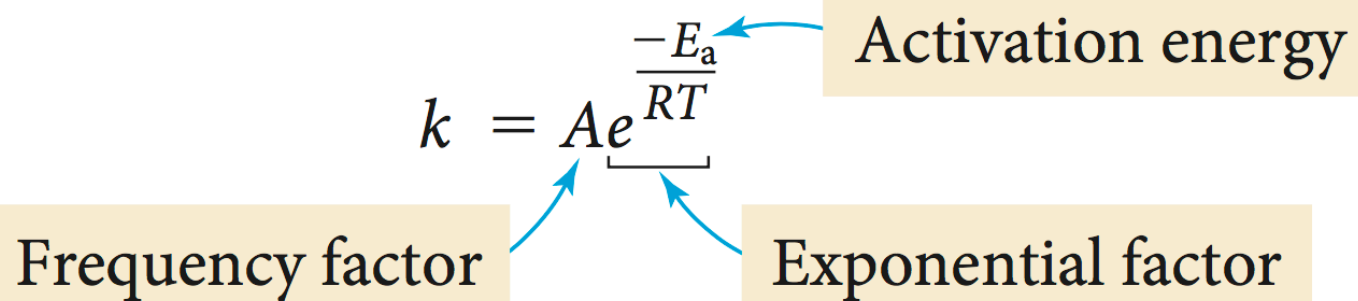
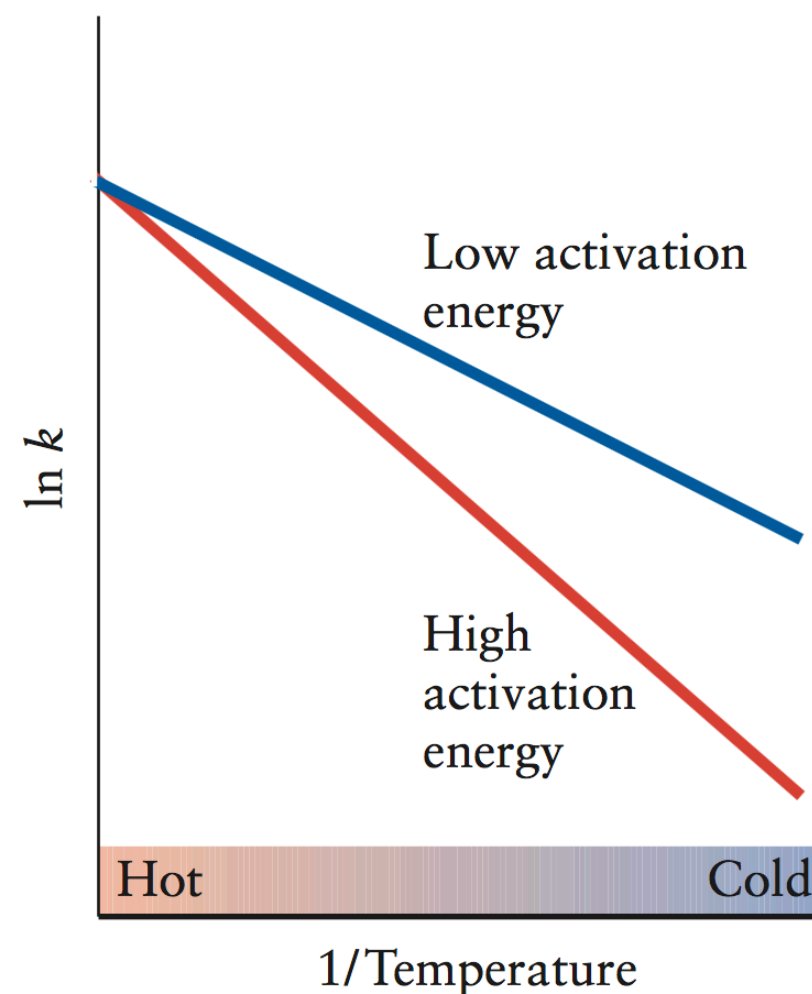
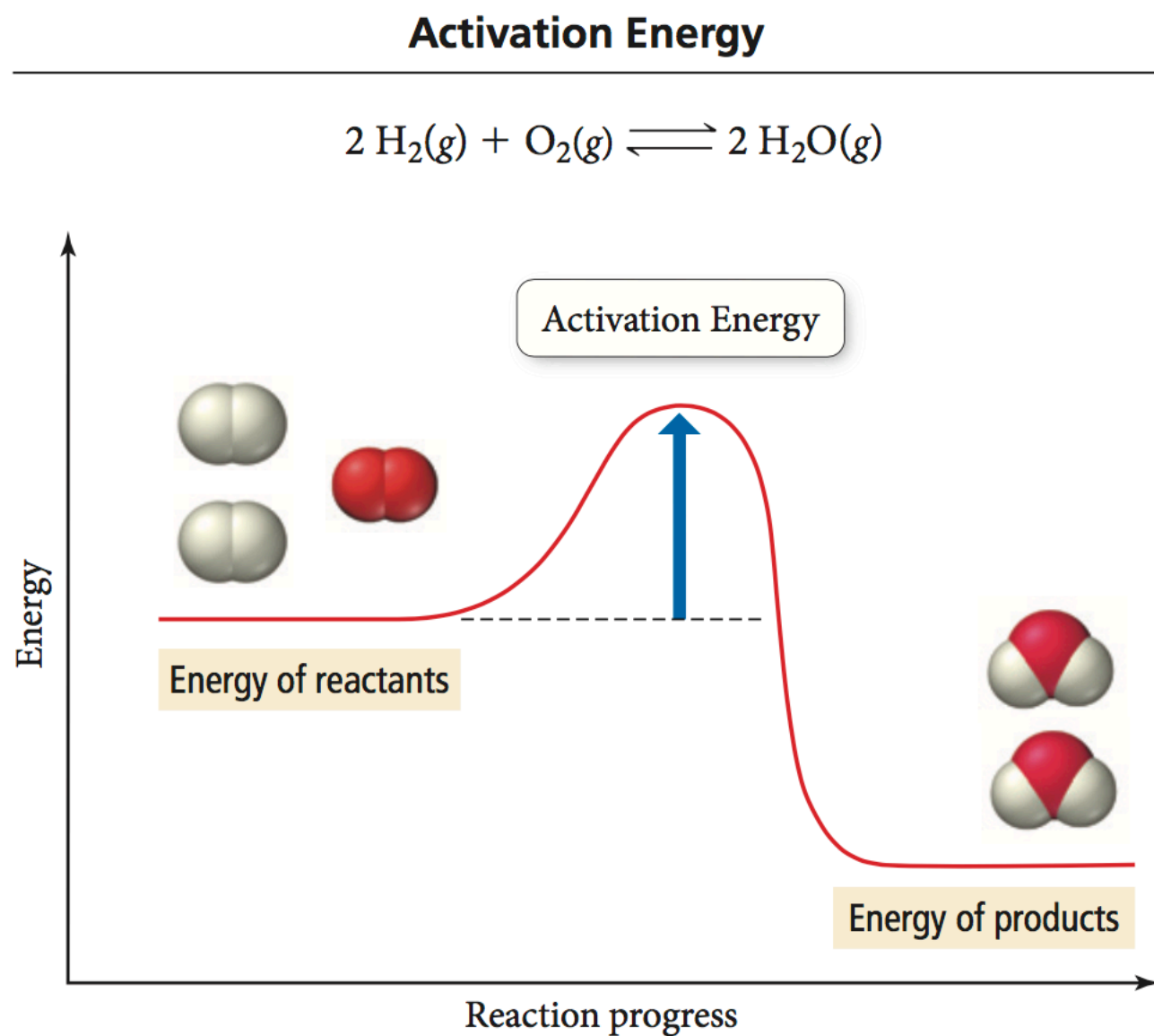
- Reactions that give a straight line when $\ln k$ is plotted against $1/T$ are said to show **Arrhenius behavior**



Temperature effect (2): Arrhenius-eq



Temperature effect (3)



the higher the activation energy, the stronger is the temperature dependence of the rate constant.

Collision theory

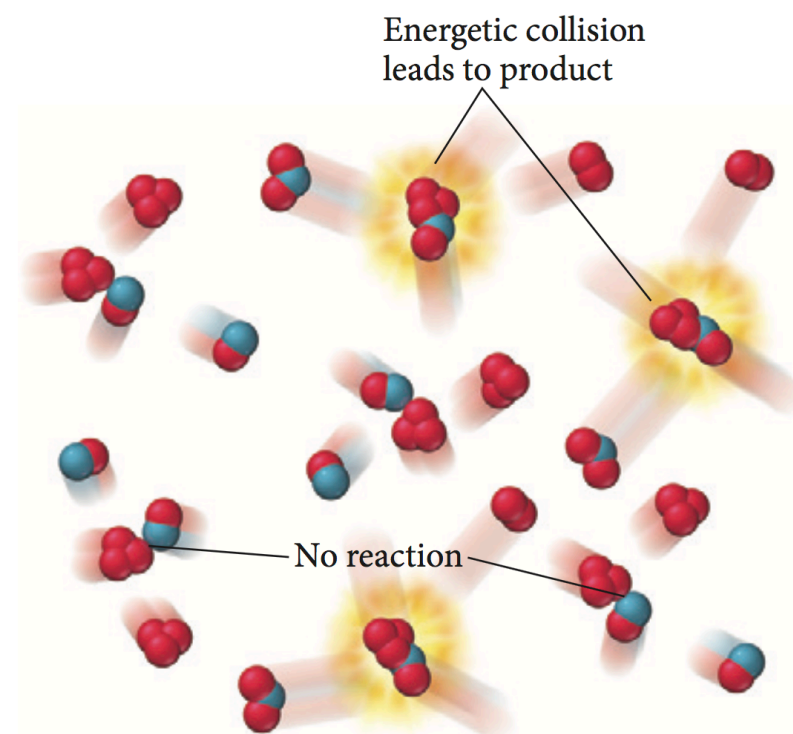
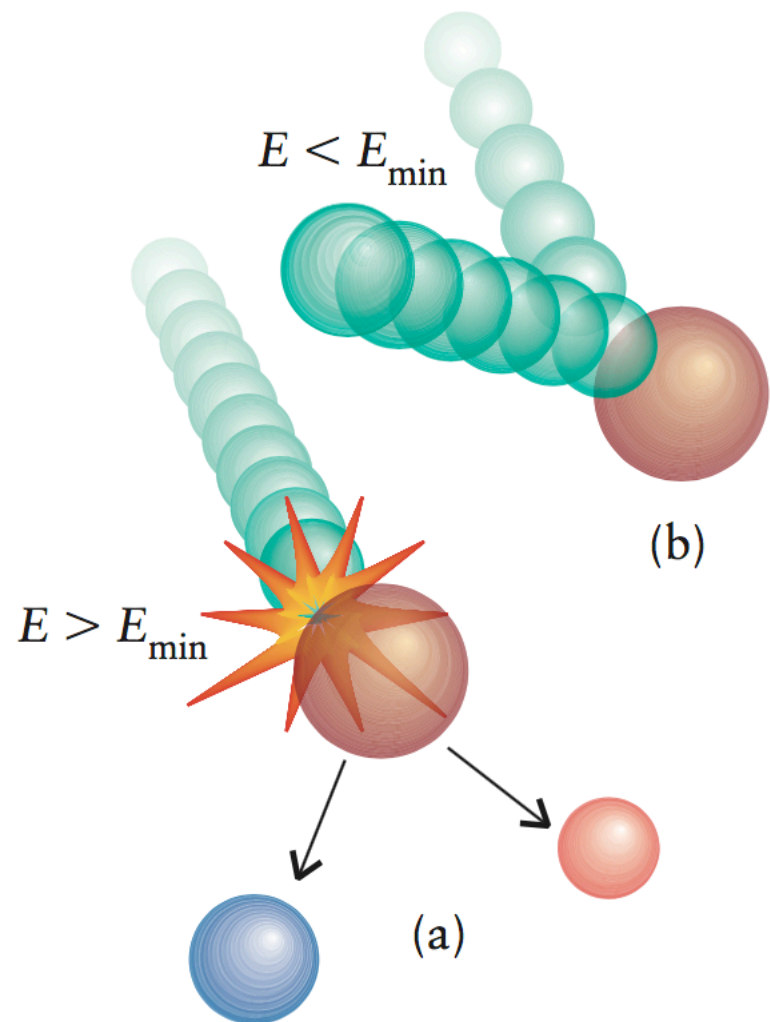
Ready to build a model of how chemical reactions take place at the molecular level. Needs to account for:

- i) T-dependence of the rate coefficients (Arrhenius)
- ii) Reveal the significance of the Arrhenius parameters (A and activation energy)

Collision theory (molecules are billiard balls)

We need to know:

- i) the rate at which molecules collide
- ii) the fraction of those collisions that have at least the energy E_{\min} required for reaction to occur.

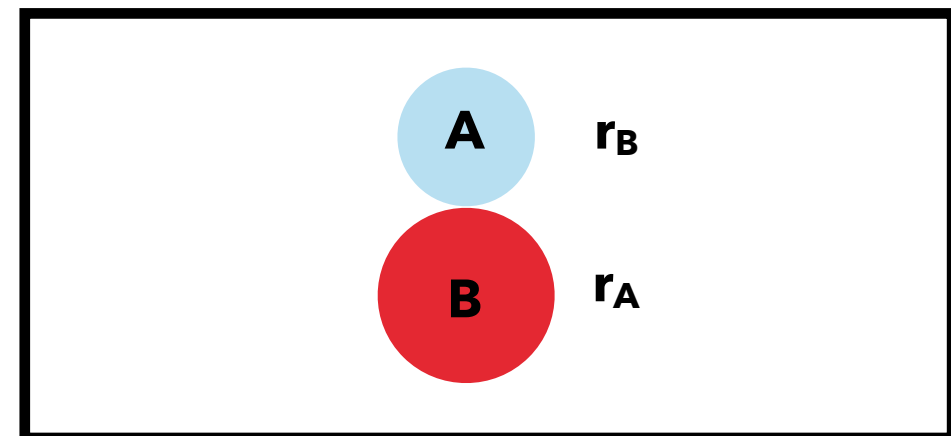
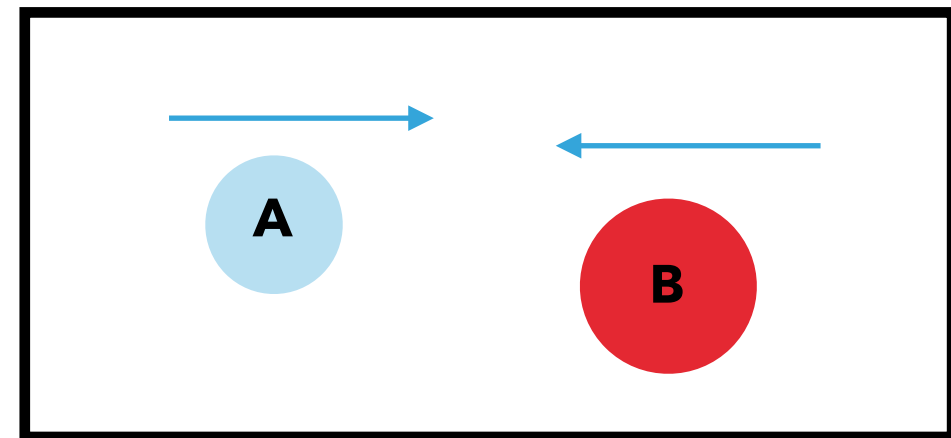


Collision theory (Boltzmann distribution)

Rate of reaction = collision frequency \times fraction with sufficient energy
 $= \sigma \bar{v}_{\text{rel}} N_A^2 [A][B] \times e^{-E_{\text{min}}/RT}$

Simple hard sphere model

$$\sigma = \pi (r_A + r_B)^2$$



Collision theory (Maxwell distribution)

$$\begin{aligned}\text{Rate of reaction} &= \text{collision frequency} \times \text{fraction with sufficient energy} \\ &= \sigma \bar{v}_{\text{rel}} N_A^2 [A][B] \times e^{-E_{\text{min}}/RT}\end{aligned}$$

$$k = A e^{\frac{-E_a}{RT}}$$

The diagram shows the Arrhenius equation $k = A e^{\frac{-E_a}{RT}}$ with three labels in yellow boxes and blue arrows pointing to the corresponding parts of the equation:

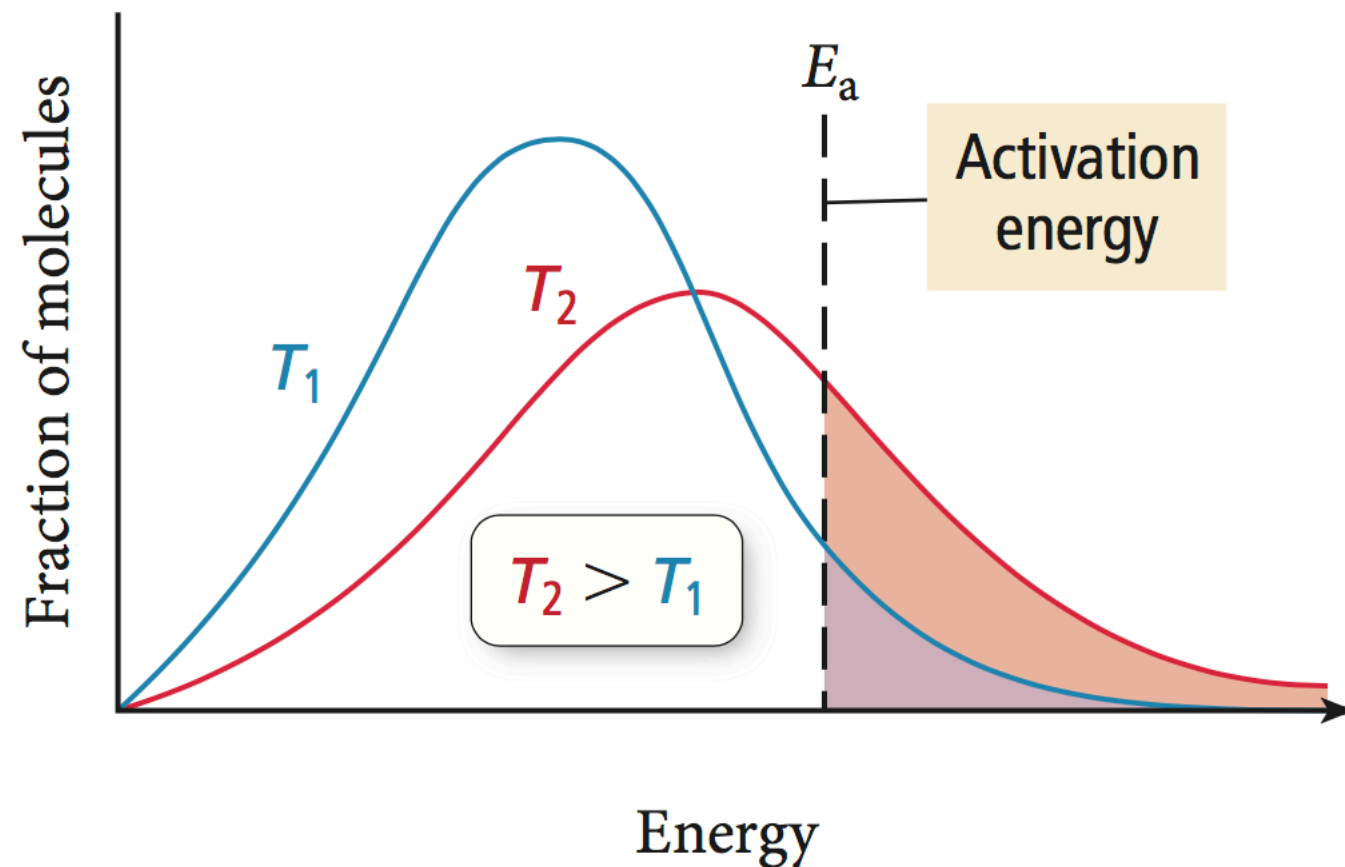
- Frequency factor** points to the letter A .
- Exponential factor** points to the entire exponential term $e^{\frac{-E_a}{RT}}$.
- Activation energy** points to the $-E_a$ in the numerator of the exponent.

- A is a measure of the rate at which molecules collide.
- The activation energy, E_a , is the minimum kinetic energy required for a collision to result in reaction.

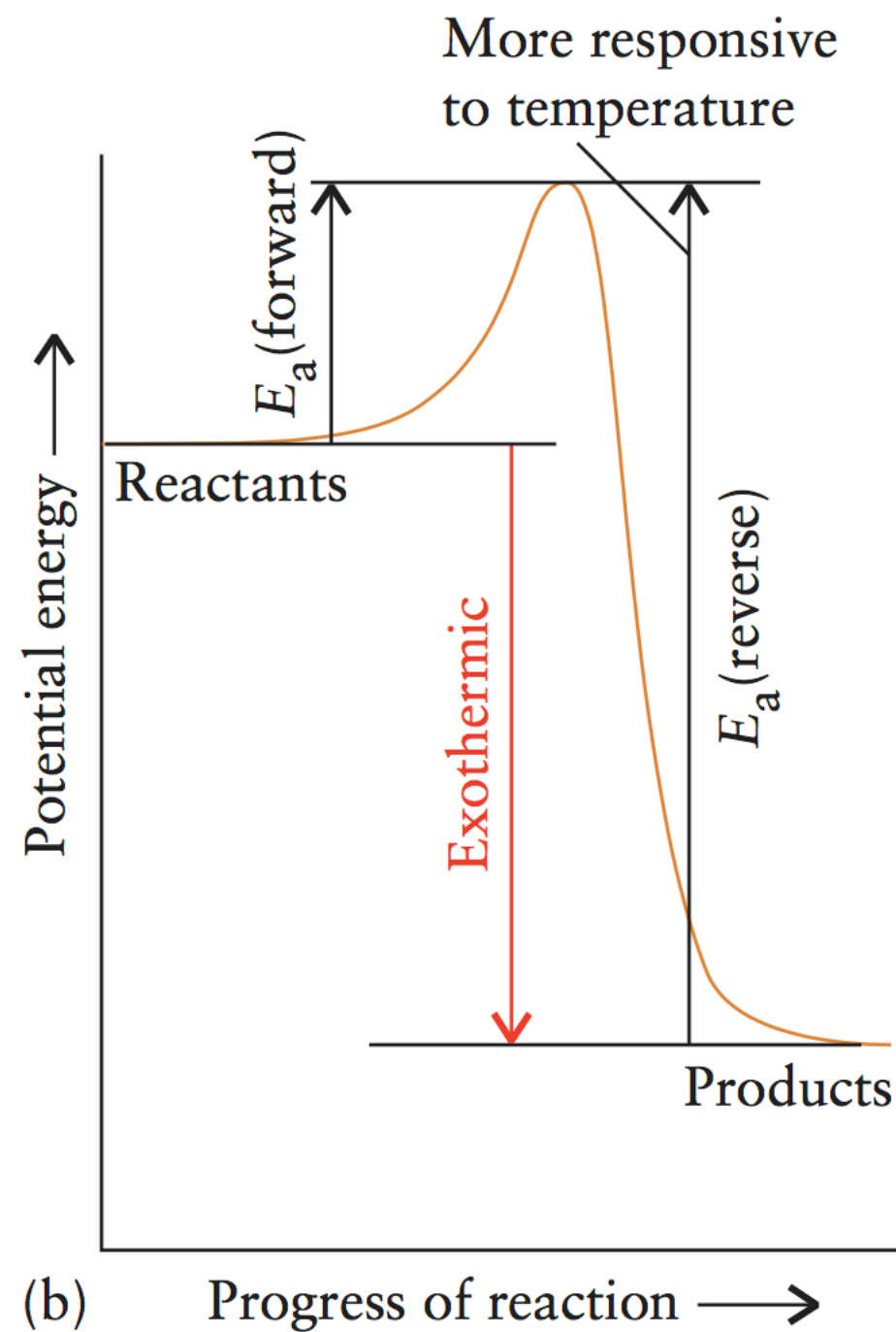
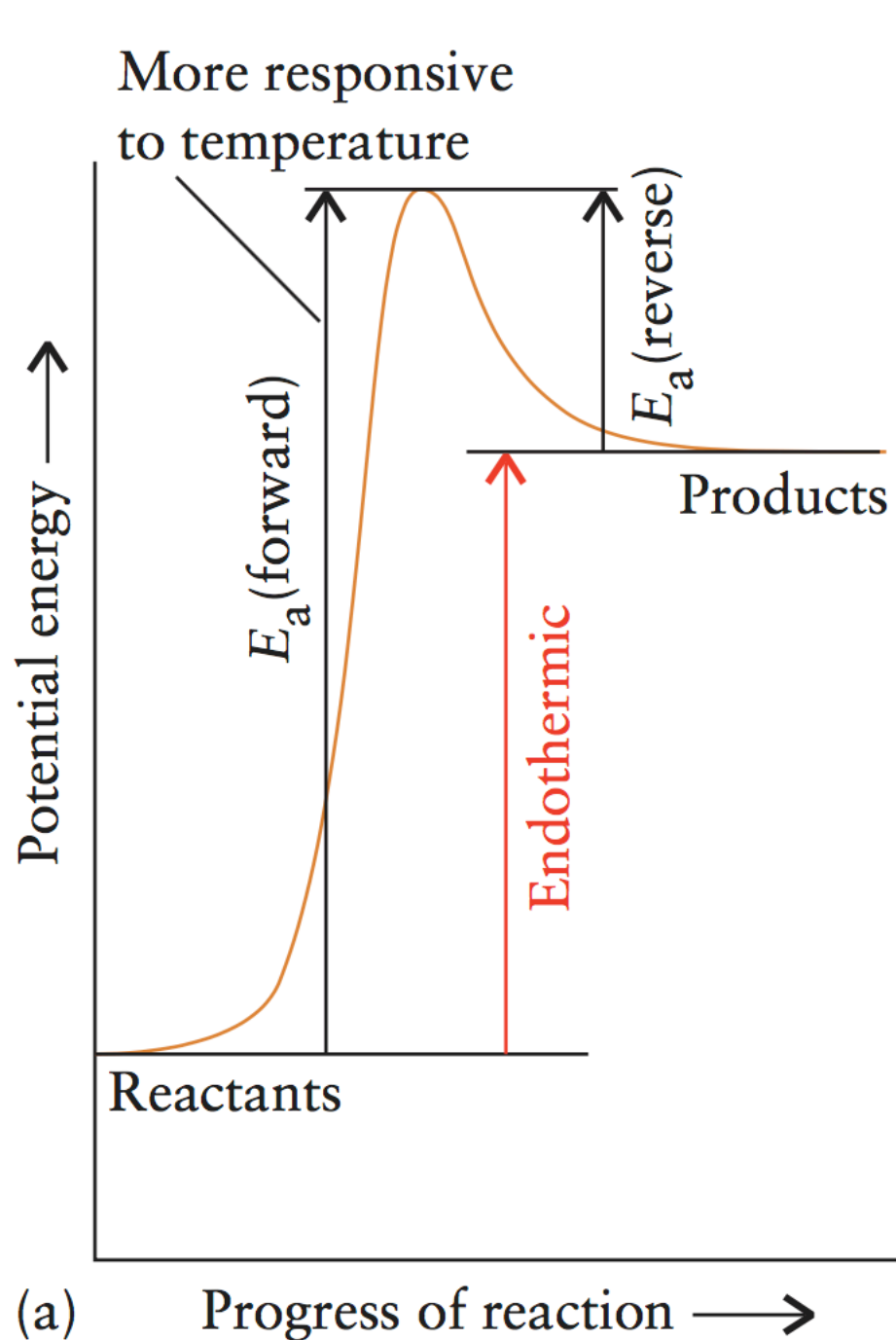
Collision theory (Maxwell distribution)

Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.



Reaction paths



Steric factor correction

$$\begin{aligned} \text{Rate of reaction} &= \text{collision frequency} \times \text{fraction with sufficient energy} \\ &= \sigma \bar{v}_{\text{rel}} N_A^2 [A][B] \times e^{-E_{\text{min}}/RT} \end{aligned}$$

$$k = \overbrace{\hat{P}}^{\text{Steric requirement}} \times \overbrace{\sigma \bar{v}_{\text{rel}} N_A^2}^{\text{Collision rate}} \times \overbrace{e^{-E_{\text{min}}/RT}}^{\text{Energy requirement}}$$

RATE COEFFICIENTS IN GAS-PHASE (THERMAL EQ)

unimolecular reactions: $A \rightarrow C$

$$k = \sigma v$$

$$-\frac{dn(A)}{dt} = k n(A) = \frac{dn(C)}{dt}$$

- ▶ The above formulation is valid if sigma is velocity-independent
- ▶ Normally: we have a distribution of speed

$$k(T) = \langle \sigma v \rangle = \int_0^{\infty} \sigma(v) v f(v) dv$$

RATE COEFFICIENTS IN GAS-PHASE (THERMAL EQ)

- ▶ This obeys a Maxwell-Boltzmann distribution

$$f(v)dv = 4\pi v^2 \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{\mu v^2}{2k_B T} \right) dv$$

$$k(T) = \langle \sigma v \rangle = 4\pi \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \int_0^\infty \sigma(v) v^3 \exp\left(-\frac{\mu v^2}{2k_B T} \right) dv$$

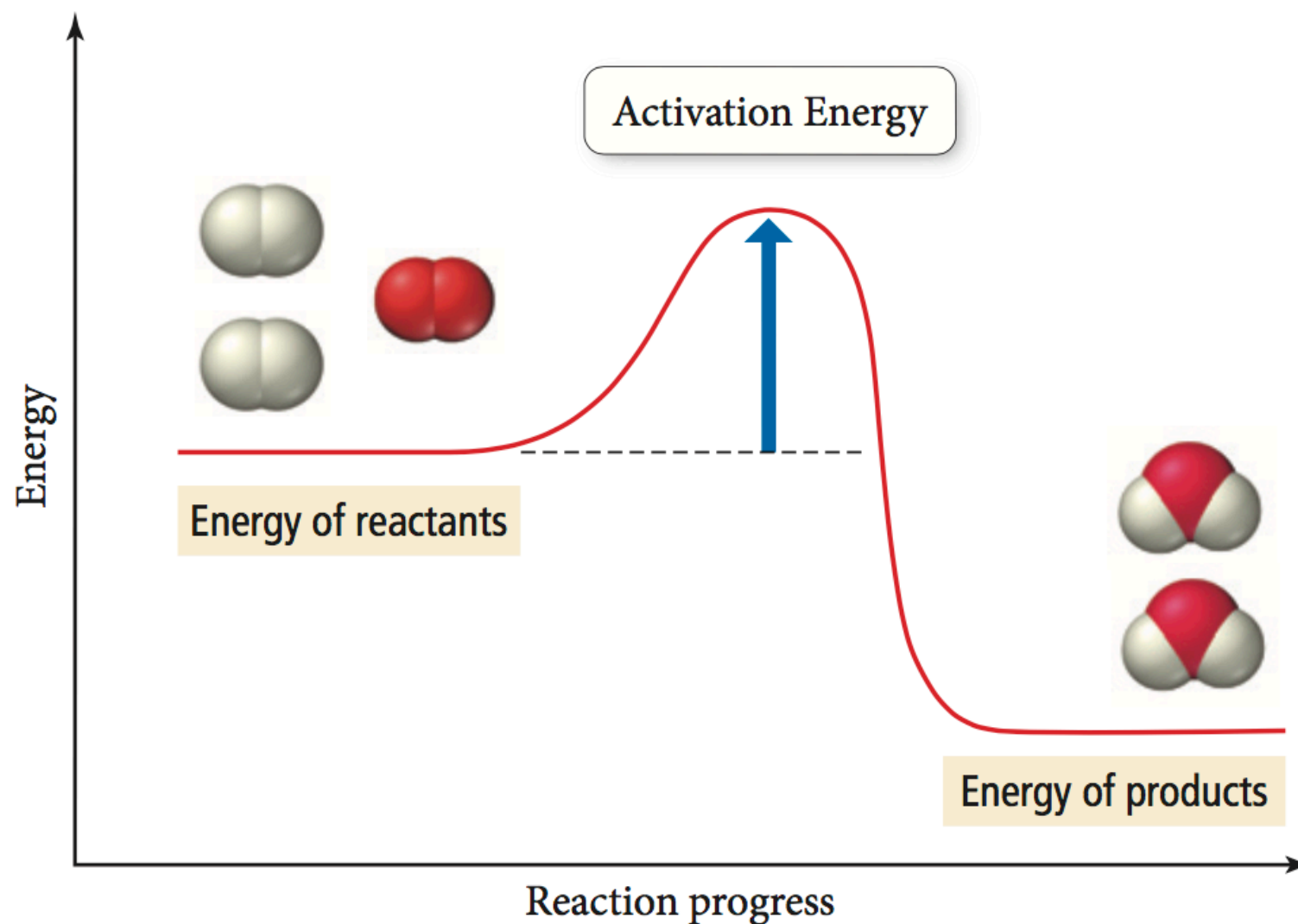
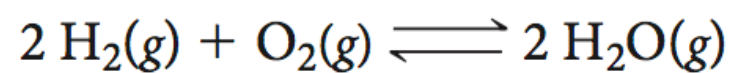
RATE COEFFICIENTS ARE KEY PARAMETERS (BUT CAUTION)

How to determine $k(T)$?

- ▶ Experimental (lucky)
- ▶ Langevin (estimate)
 - ▶ valid for ion-molecule reactions
 - ▶ "exothermic", i.e. without barrier
 - ▶ temperature independent
- ▶ Physical considerations (e.g. H=D)
- ▶ *ab initio* calculations (not always available)
 - ▶ solving the Schrödinger equation (2nd order coupled PDEs)

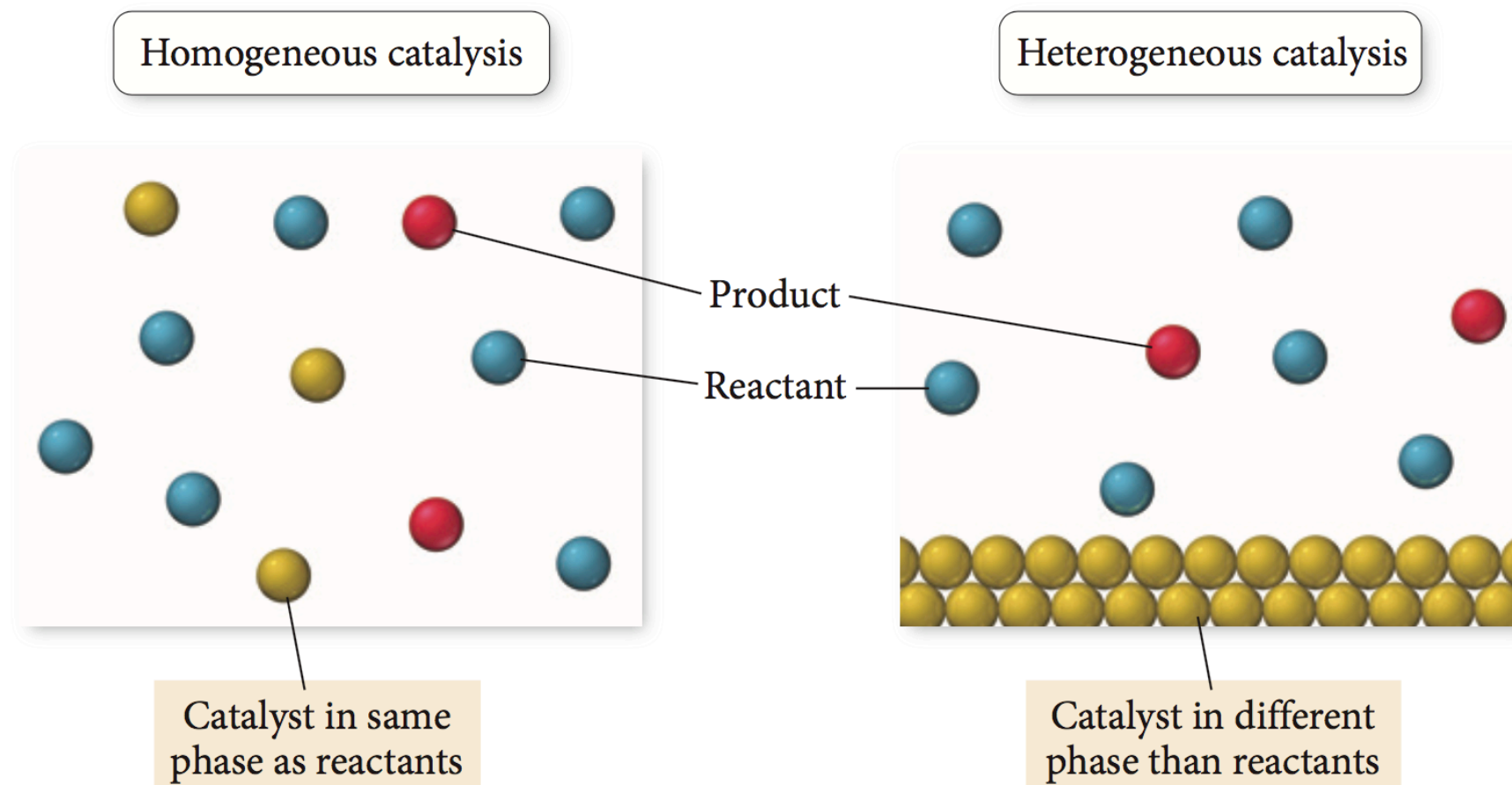
Can a reaction be accelerated?

Activation Energy

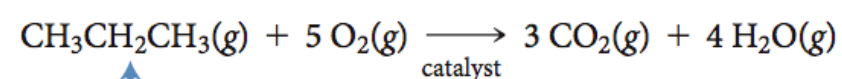
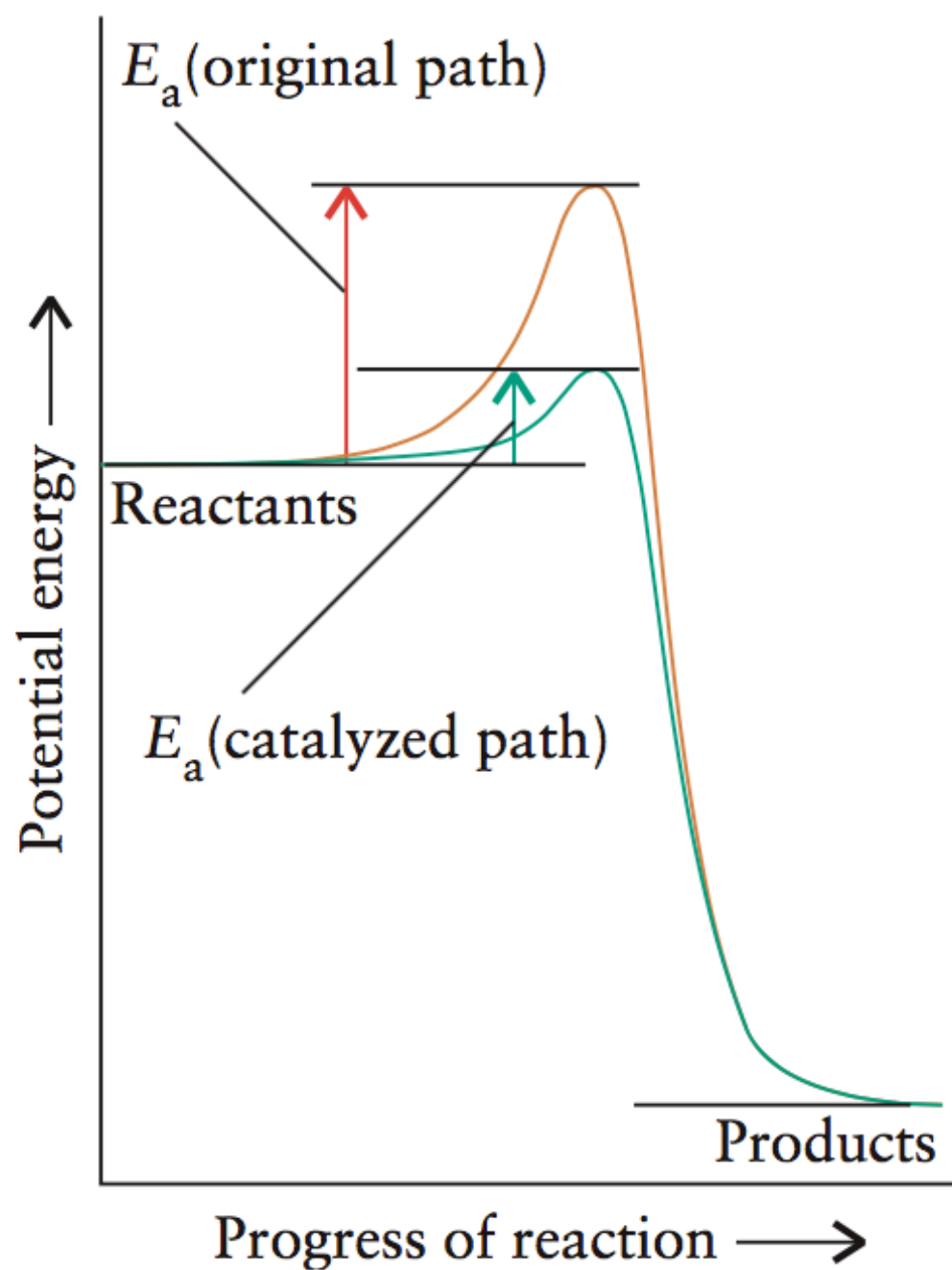


Catalysis

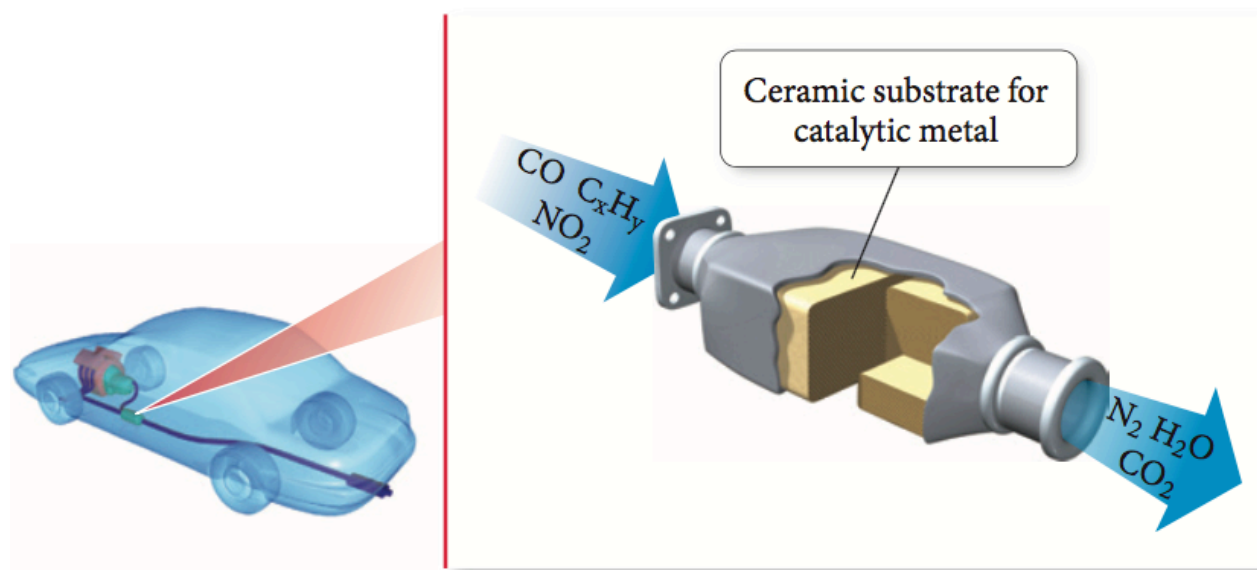
- **Catalyzers**
 - Increase the speed of a reaction
 - In some cases, allows it to occur



Effect of catalyzer on the reaction path

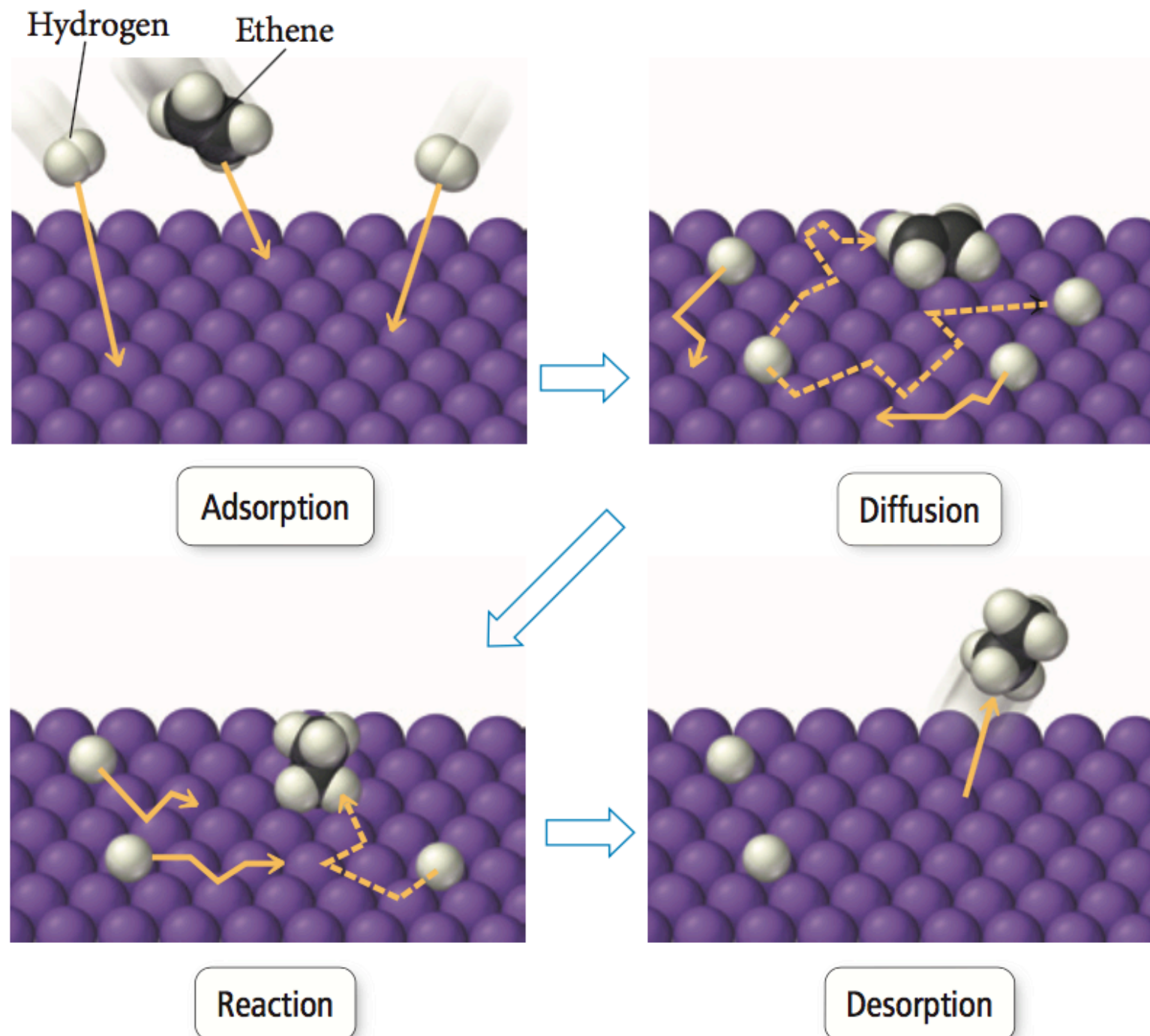


Fuel fragment

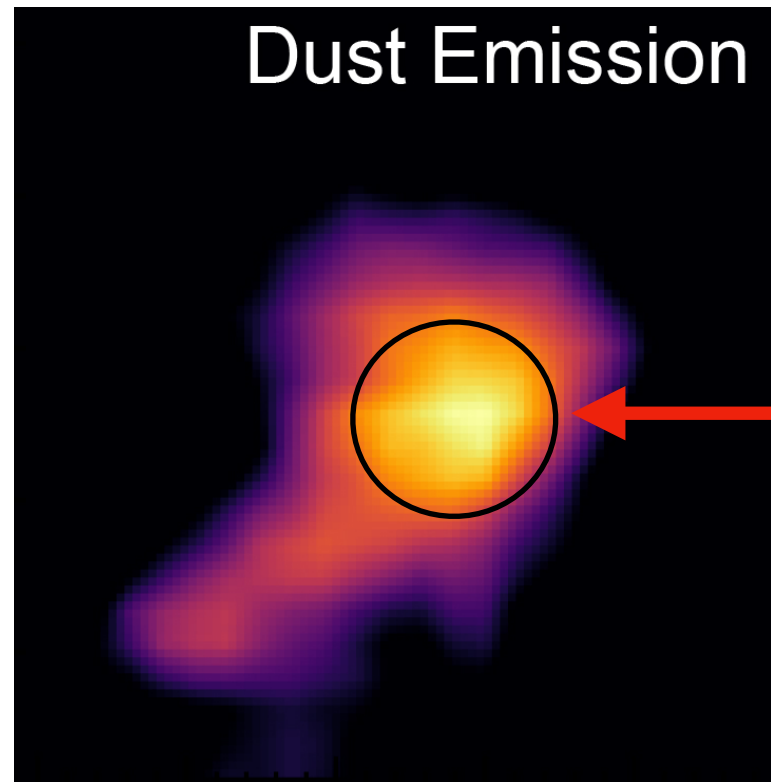
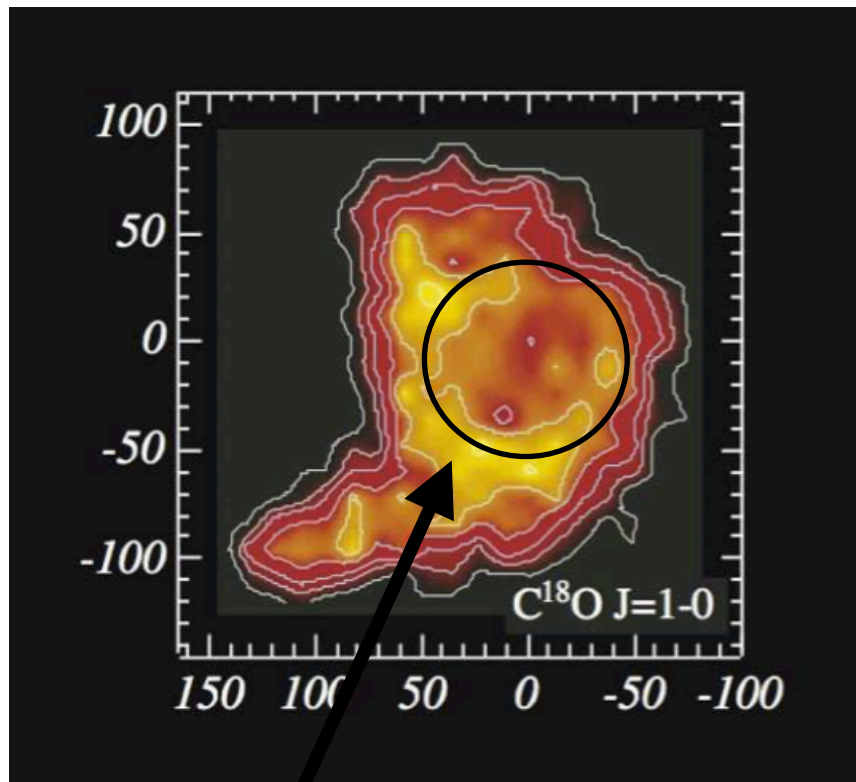


Dust grains: role as catalyzers

Heterogeneous Catalysis



Dust grains drive reactions



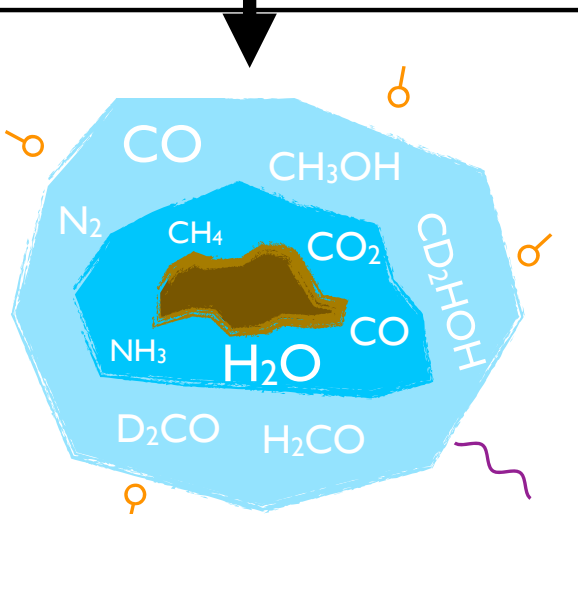
Methanol formation @ 10 K

High density and cold

CO

1st step

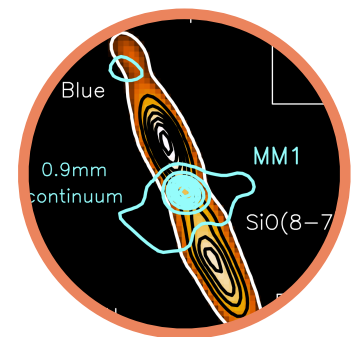
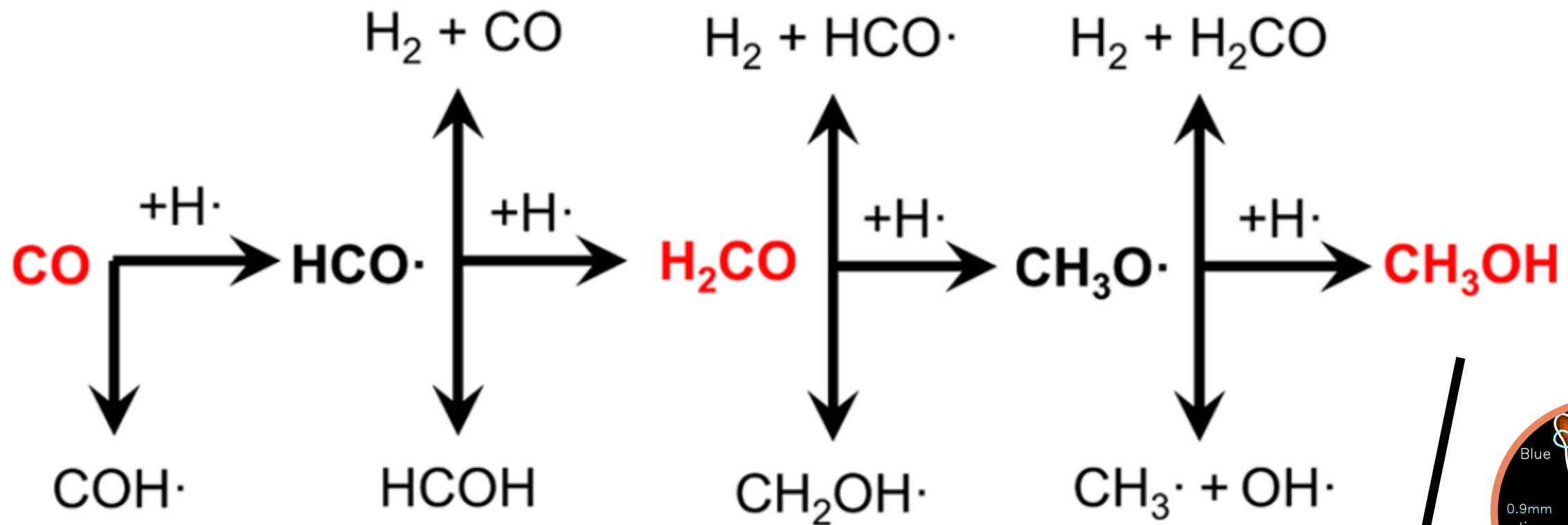
Adsorption/Freeze-out



Dust grains drive reactions

Methanol formation @ 10 K

Hydrogenation process
2nd step

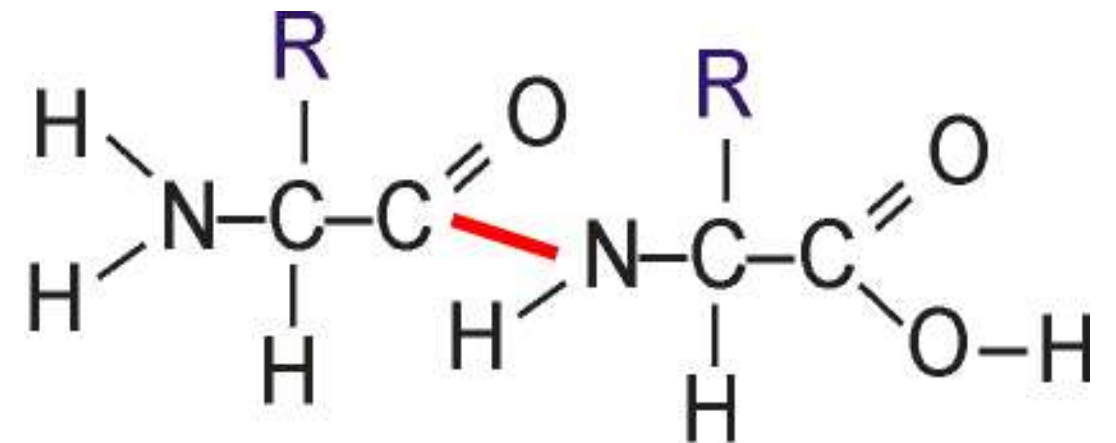
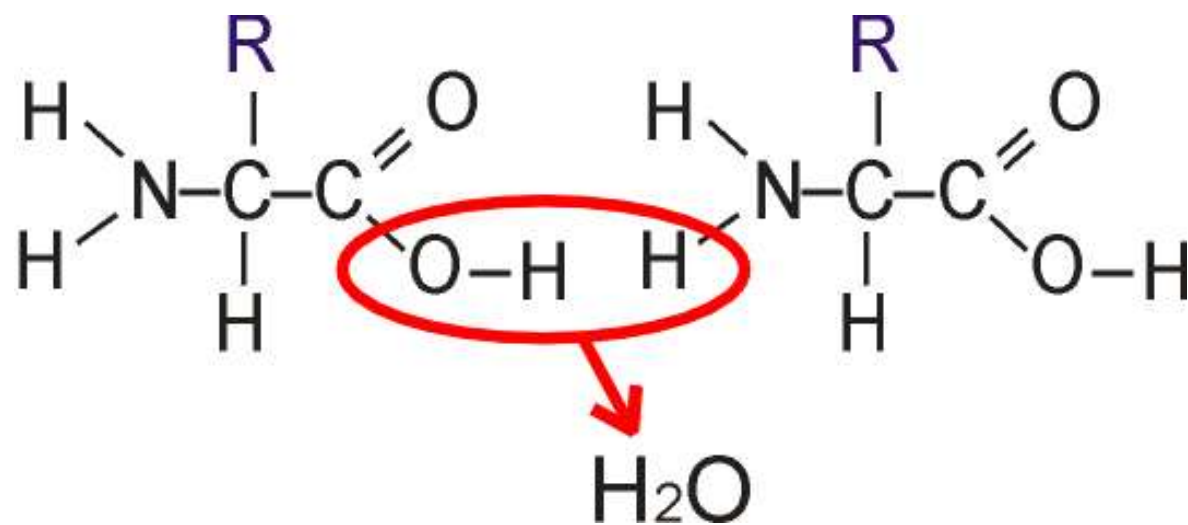


When a protostar forms the T increases and the molecules desorb going back into the gas phase.

Life: prebiotic molecules

To form a protein a standard mechanism is polymerization of amino acids

Polymerization is a loss of water which leads to condensation of two or more amino acids (formation of polypeptide)



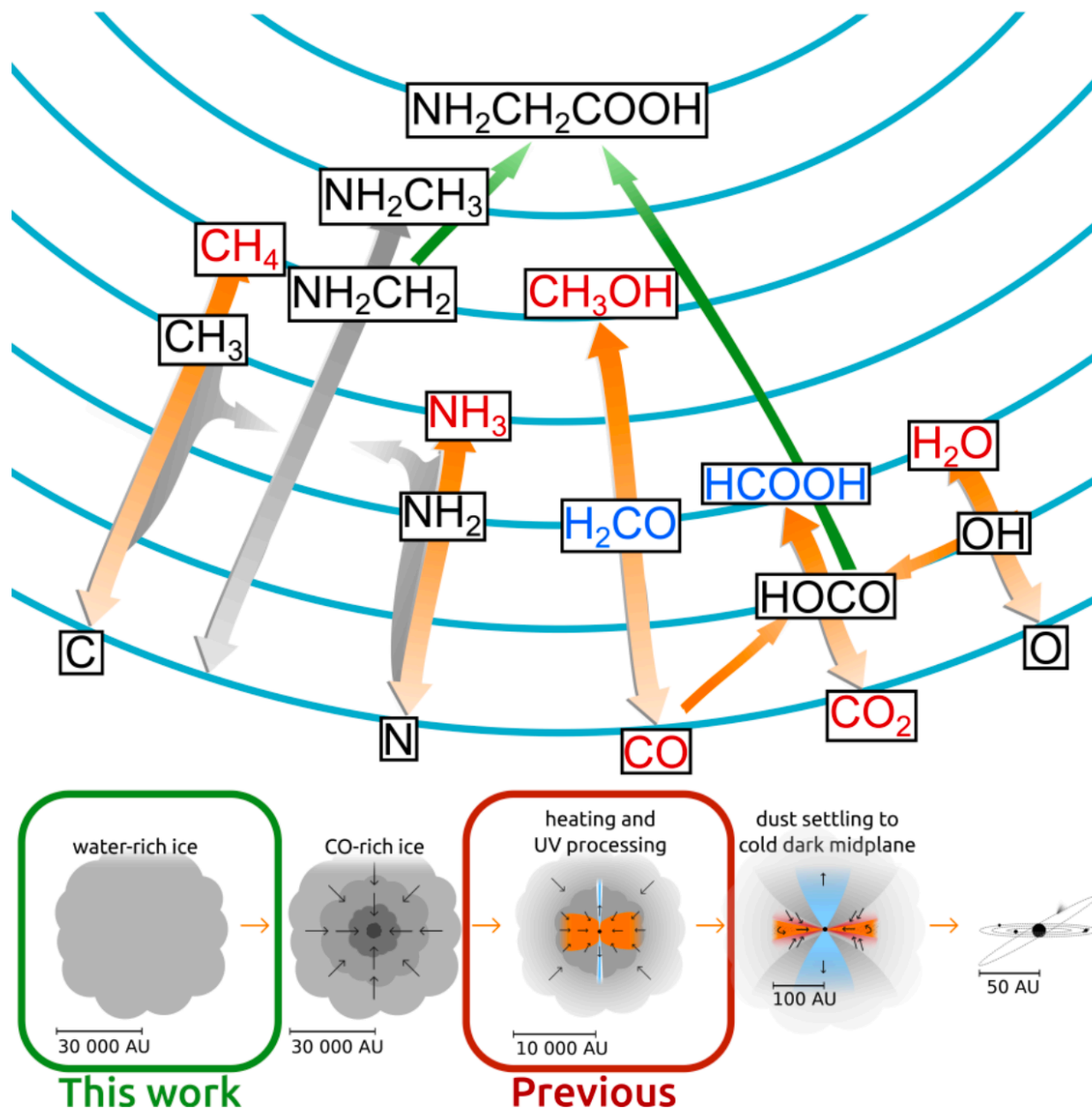
Peptide bond -
links Carbon of acid group
to Nitrogen of amine group

THIS PROCESS REQUIRES ENERGY

Dust grains drive reactions

S. Ioppolo et al., 2020

Glycine synthesis @ 10 K
(via addition/abstraction reactions)



ENERGETIC ROUTES

Old paradigm: need of energetic paths:
Via UV, CRs, or high-T environment

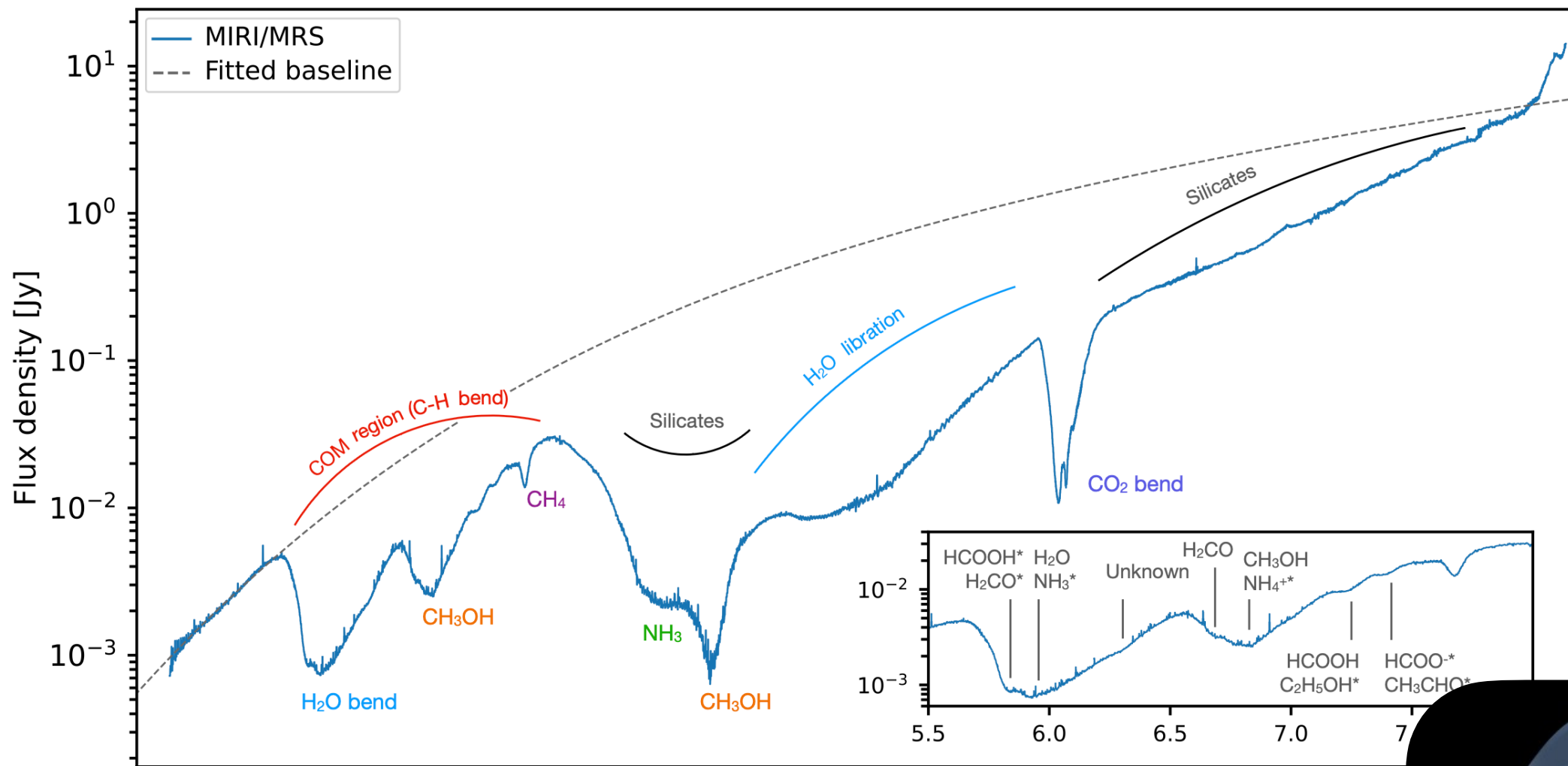
But these conditions can also alter the
products of the reaction

NON-ENERGETIC ROUTES

This new experiment shows that is
possible to form simple amino acids at
low temperatures

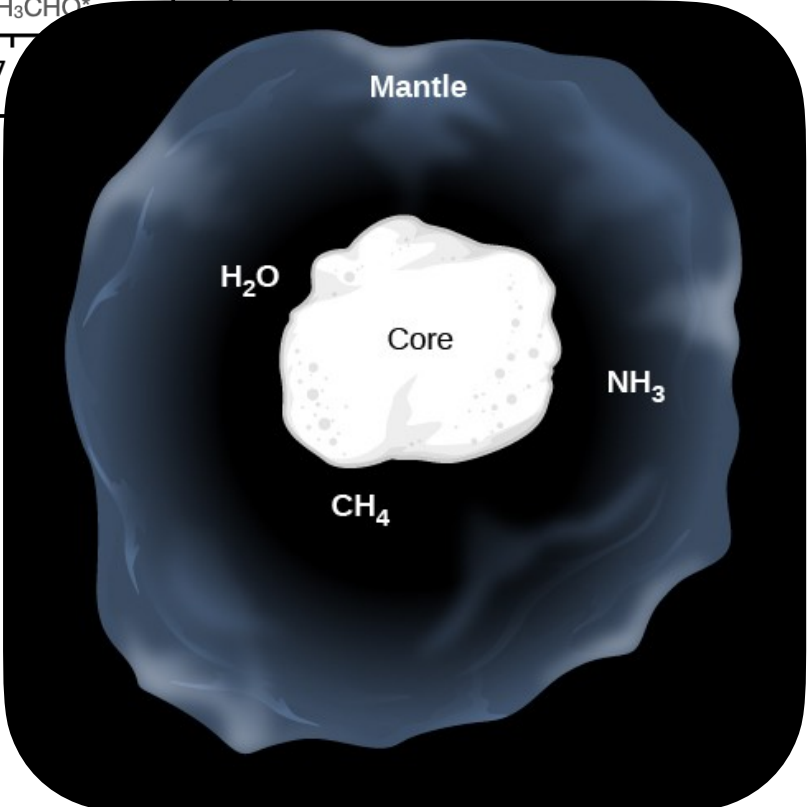
Dust grains drive reactions

S. Ioppolo et al., 2020



Co-deposit CO and methylamine

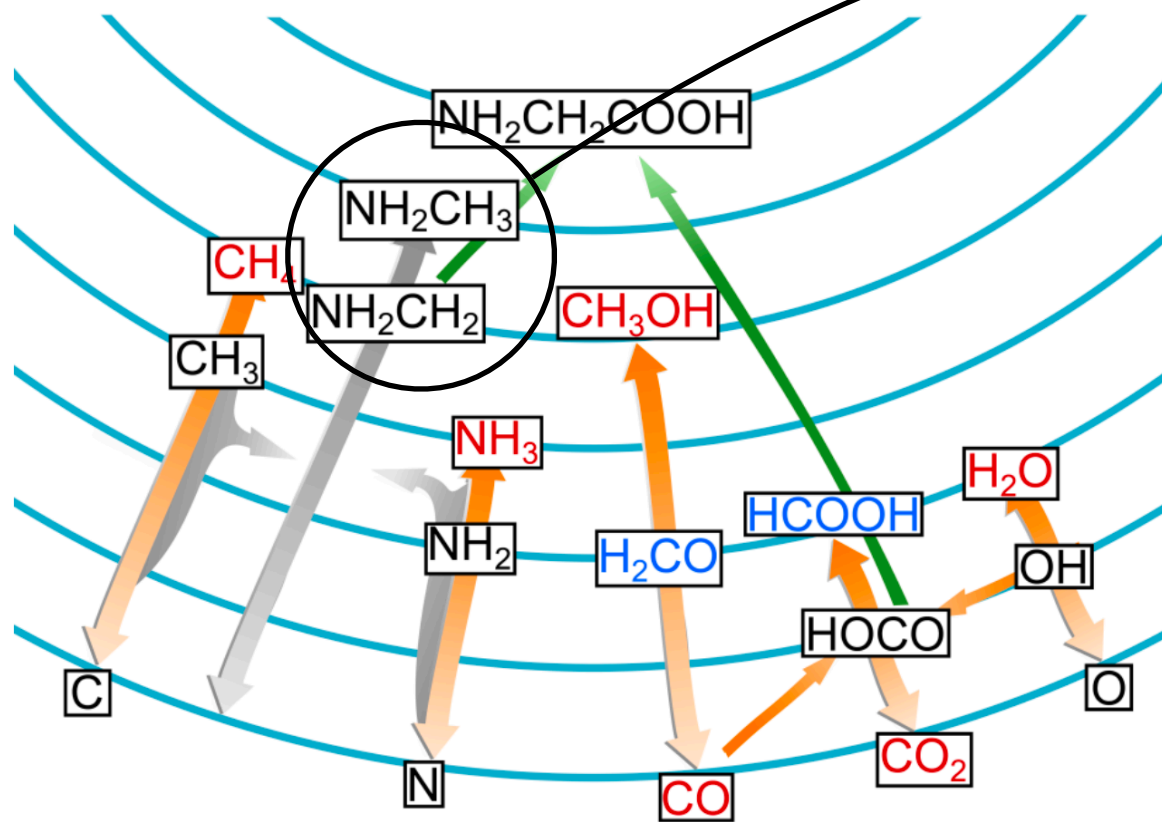
Formation of methylamine has been proved by standard abstraction/addition reaction of standard ices



Dust grains drive reactions

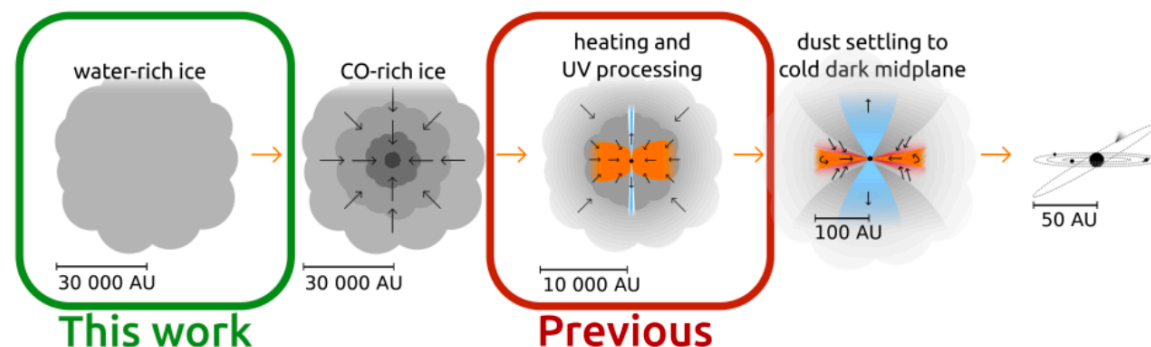
S. Ioppolo et al., 2020

Glycine synthesis @ 10 K
(via addition/abstraction reactions)



Precursors of glycine can form on this mix of ices

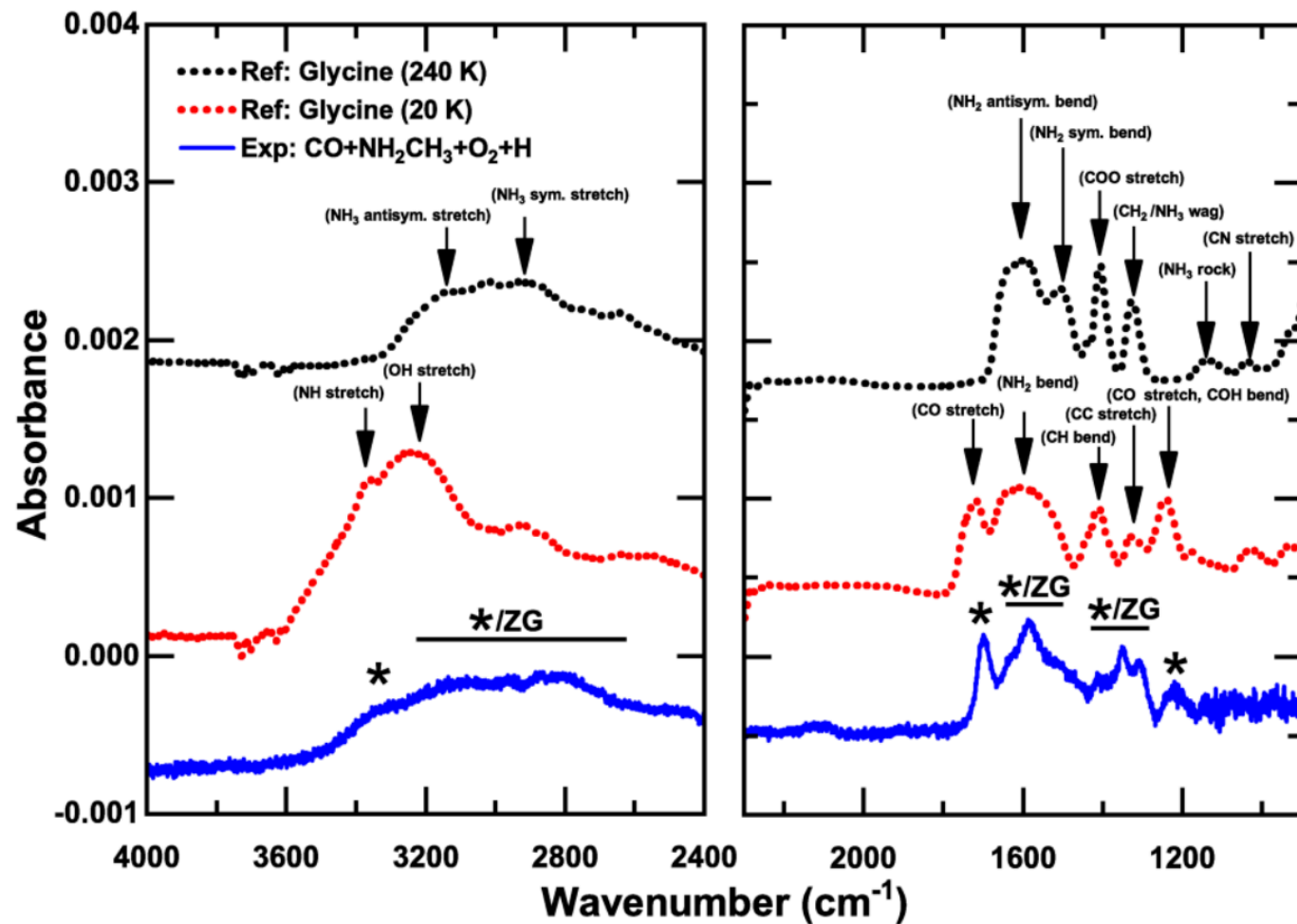
Glycine is finally produced via radical-radical reactions (very fast) between NH₂CH₃ and HOCO



Dust grains drive reactions

S. Ioppolo et al., 2020

Glycine synthesis @ 10 K
(via addition/abstraction reactions)



Precursors of glycine can form on this mix of ices

Glycine is finally produced via radical-radical reactions (very fast) between NH₂CH₃ and HOCO

They measure the IR spectrum of glycine on ices via Reflection Absorption InfraRed (RAIR)

And corroborate via Temperature Programmed Desorption

Dust grains drive reactions

ANOTHER NON-ENERGETIC ROUTES

Demonstrated by a mix of experiments and theoretical results

Alternative to standard polymerization of amino acids

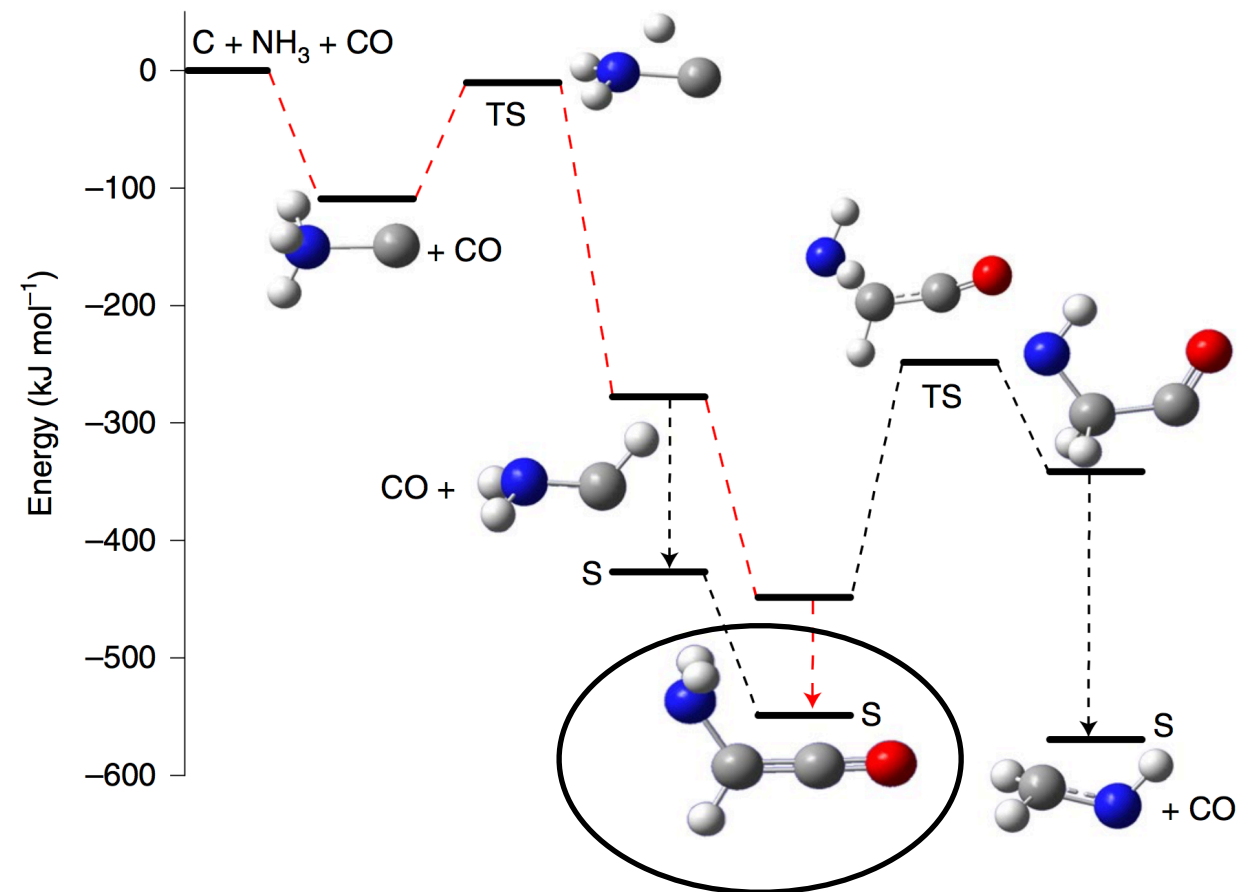
This is supposed to happen in translucent clouds (where C is still available)

**AMINOKETENE
FORMATION IS
BARRIERLESS**



Krasnokutski *et al.*, 2021

Glycine synthesis @ 10 K
(via aminoketene)



Followed by polymerization to form polyglycine

SEARCHING FOR MOLECULES IS NOT EASY



Where's Wally? In Space

SEARCHING FOR MOLECULES IS NOT EASY

Propadienone most stable configuration, lowest energy

Thermodynamics says this should be the most abundant!

- Hydrogen (H)
- Carbon (C)
- Oxygen (O)



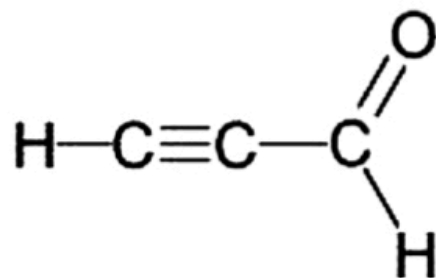
Waldo Isomer



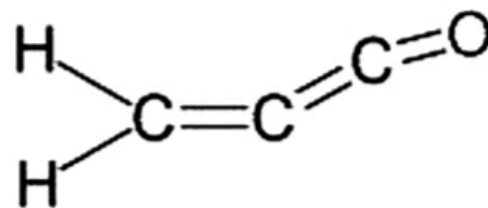
Waldo



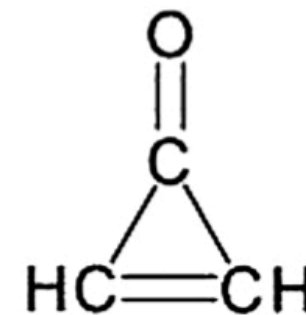
Waldo Isomer



propynal
HCCCHO



propadienone
CH₂CCO



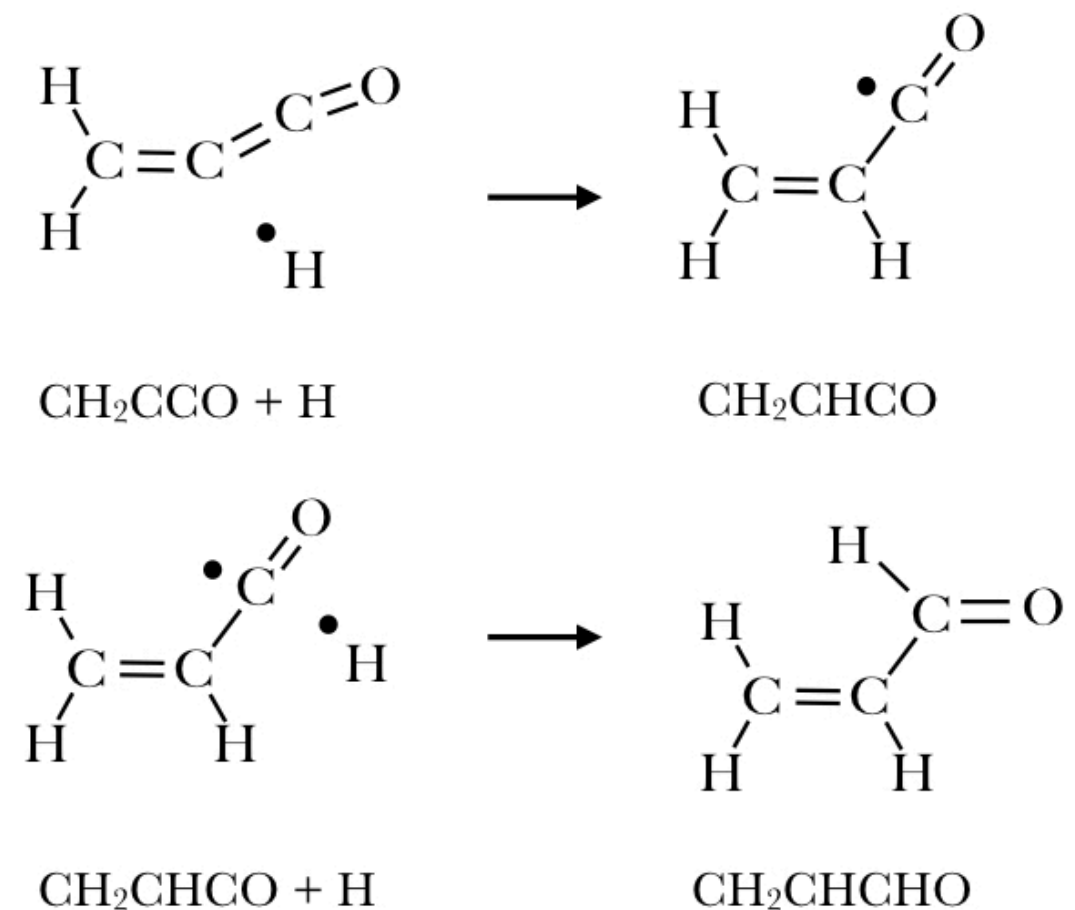
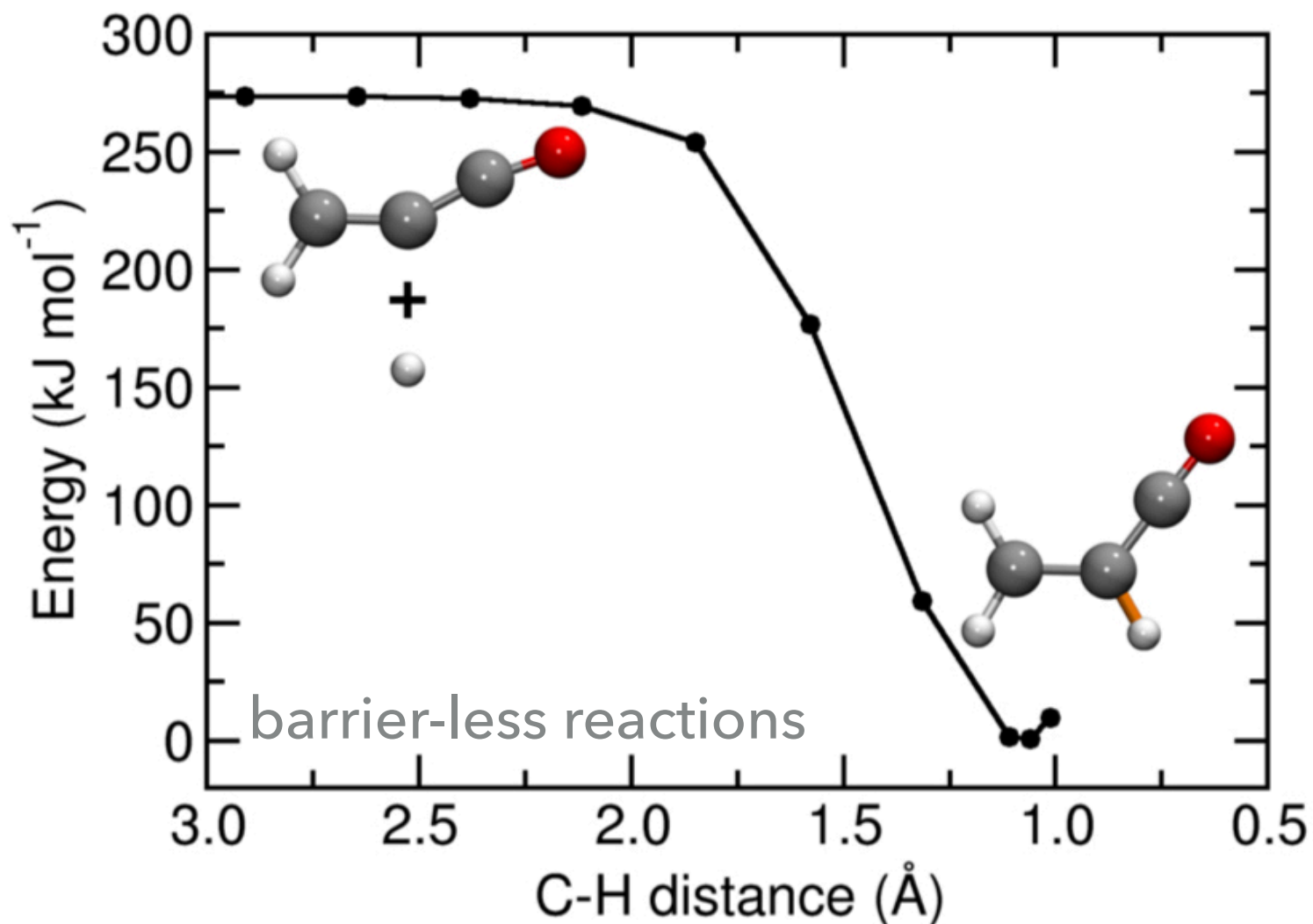
cyclopropenone
c-H₂C₃O

ISOMERS

SEARCHING FOR MOLECULES IS NOT EASY

Through quantum mechanics methodology you can determine the most stable structures of molecules and their associated energies.

CH₂CCO can react with two hydrogen atoms to form propenal (CH₂CHCHO).



SEARCHING FOR MOLECULES IS NOT EASY

Second most stable isomer "propynal" hydrogenation is a reaction with barrier!

This explains why this isomer persists in molecular clouds and can be observed.

KINETIC THEORY

OBSERVATIONS

AGREEMENT



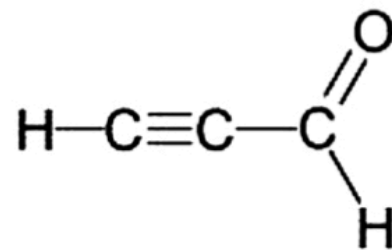
Waldo Isomer



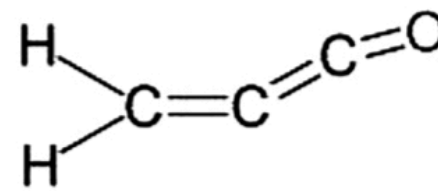
Waldo



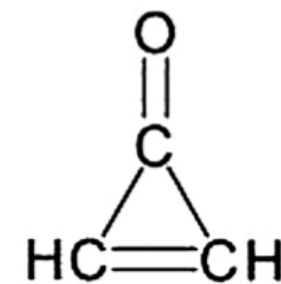
Waldo Isomer



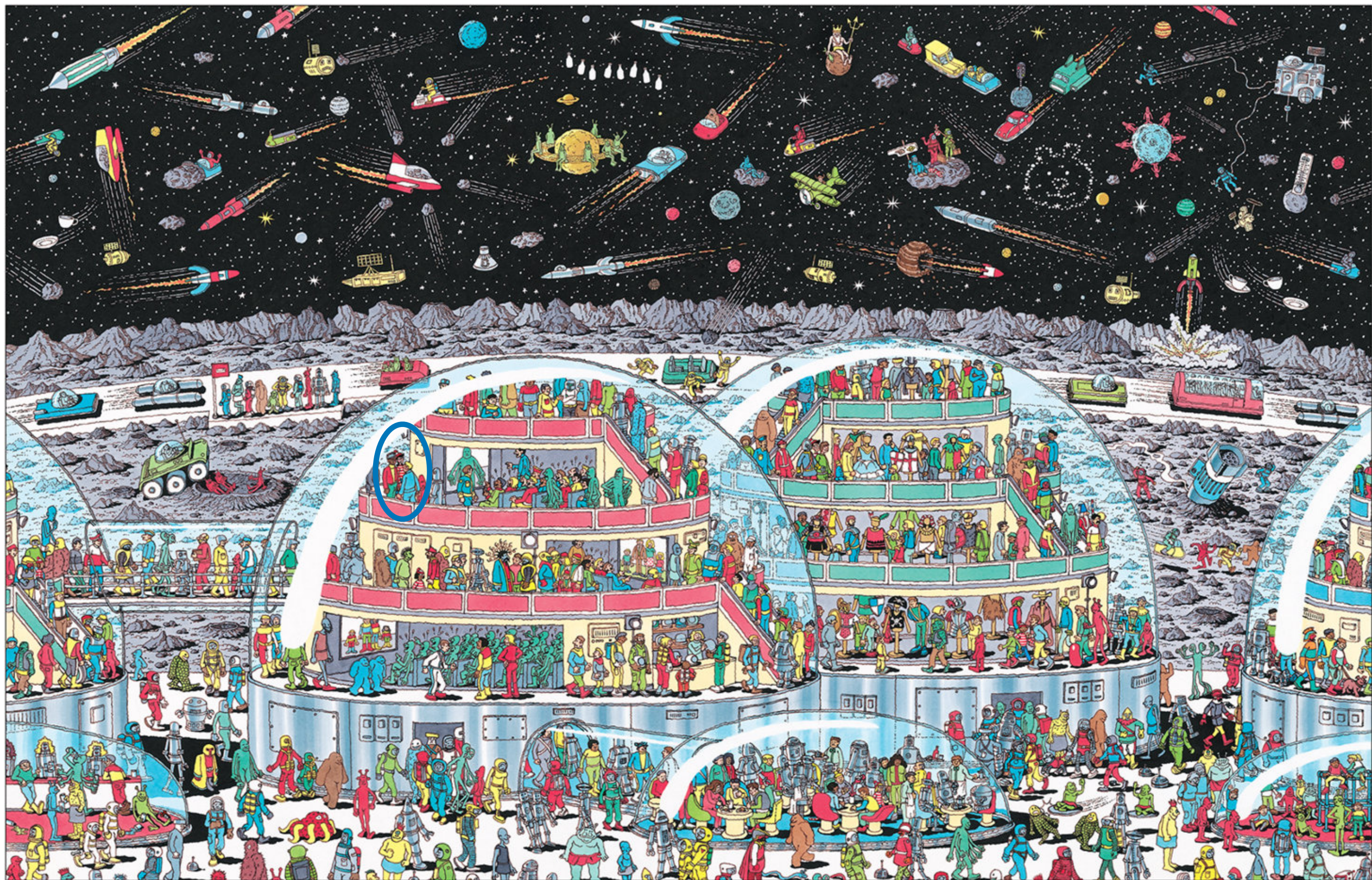
propynal
HCCCHO



propadienone
CH₂CCO



cyclopropenone
c-H₂C₃O



Where's Wally? In Space

Kinetics and Astrochemistry

- Collision theory describes how reactions occur at molecular level
- It is a fundamental tool to understand chemistry under ISM conditions
- Cross sections and rate coefficients represent the key physical quantities
- Cross sections evaluation is not always straight/possible (quantum mechanics or guesses)
- Rate equations allow to follow evolution of key species under pre-defined conditions