

**Exoplanetary Atmospheres and Habitability –
Thermodynamics, Disequilibrium and Evolution focus group
12–16 October 2015, Nice**

**Does a Possibility of Emergence of Life in
Deep Oceans of Icy Moons Meet the
Physicochemical Requirements Inferred
for Chemical Self-organization Processes?**

ROBERT PASCAL

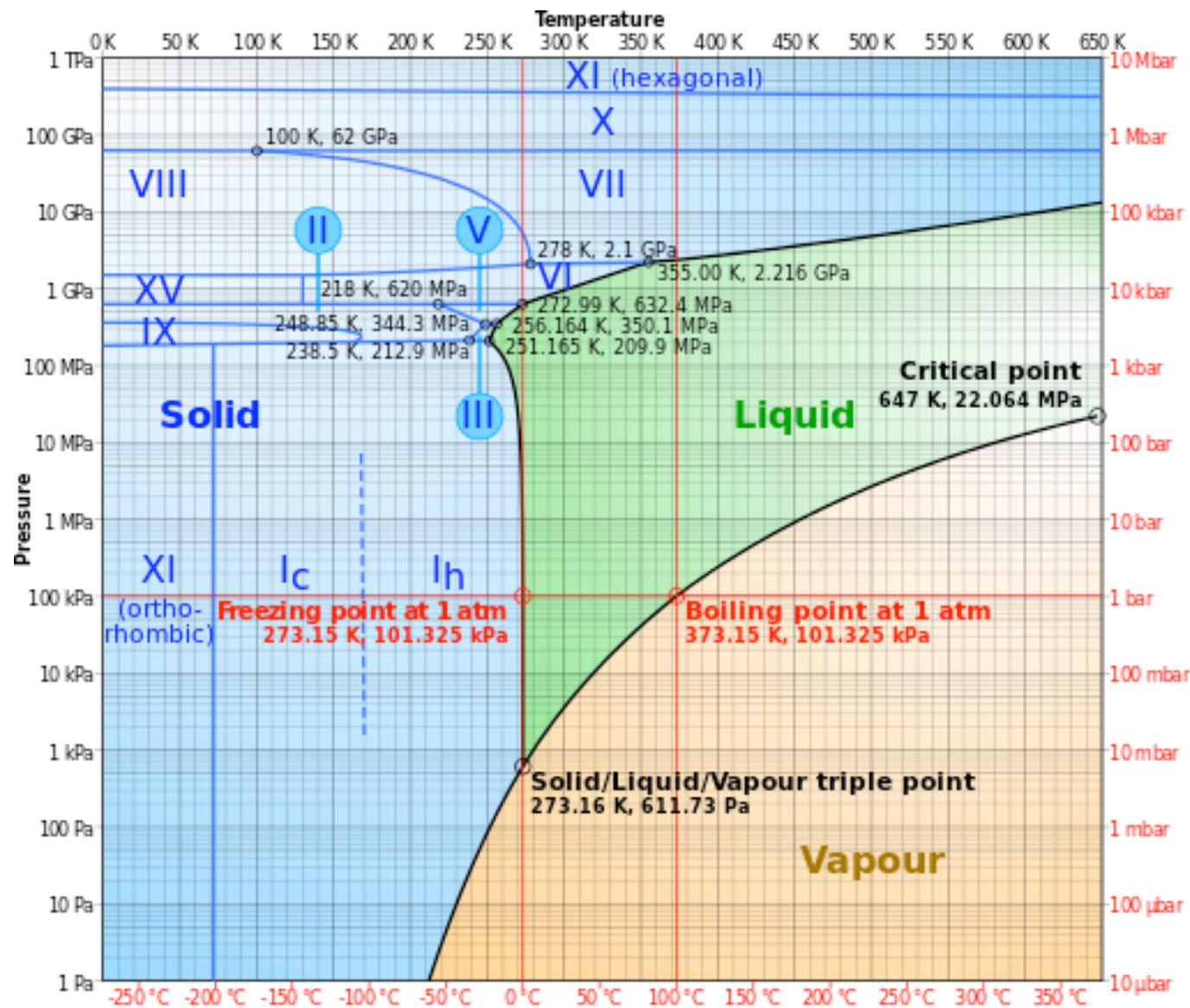
IBMM, UMR5247, CNRS — University of Montpellier



Habitability

- Baross et al. 2007 (<http://www.nap.edu/catalog/11919.html>)
 - Presence of a liquid
 - Presence of a thermodynamic disequilibrium
 - Presence of an environment capable of maintaining covalent bonds
 - Presence of a molecular system capable of supporting Darwinian evolution
- Commonly:
 - Liquid water + organic matter

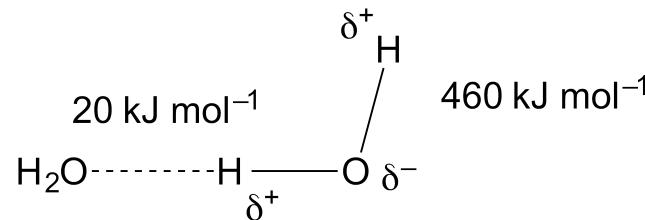
Why water as a liquid



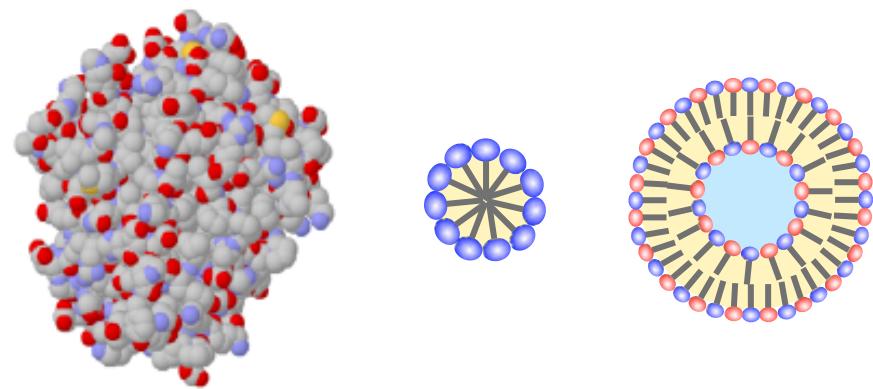
Water as a unique solvent

- The most abundant solvent in the Universe
 - Made of the most abundant reactive elements H and O

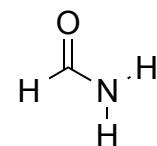
- Polarity / protic character



- Hydrophobic interactions
 - Structure formation
 - Molecular aggregates of amphiphilic molecules



- Few possible alternative solvents

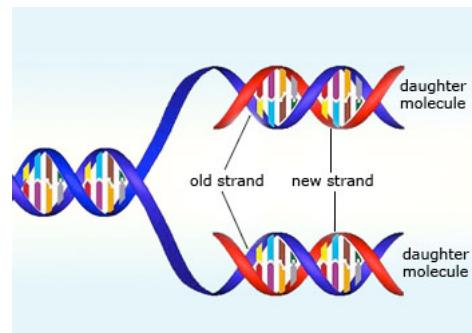


Covalent bonds

- Chemistry of reduced carbon (organic chemistry).

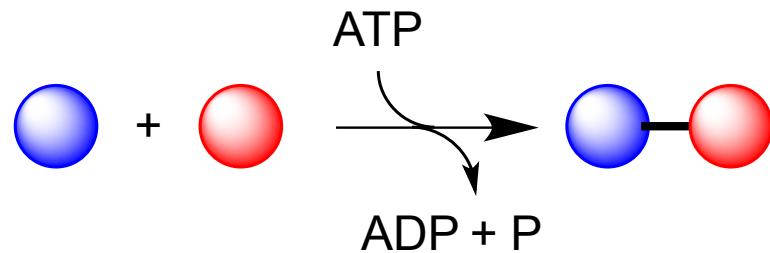
Darwinian evolution

- Replication, variability and function



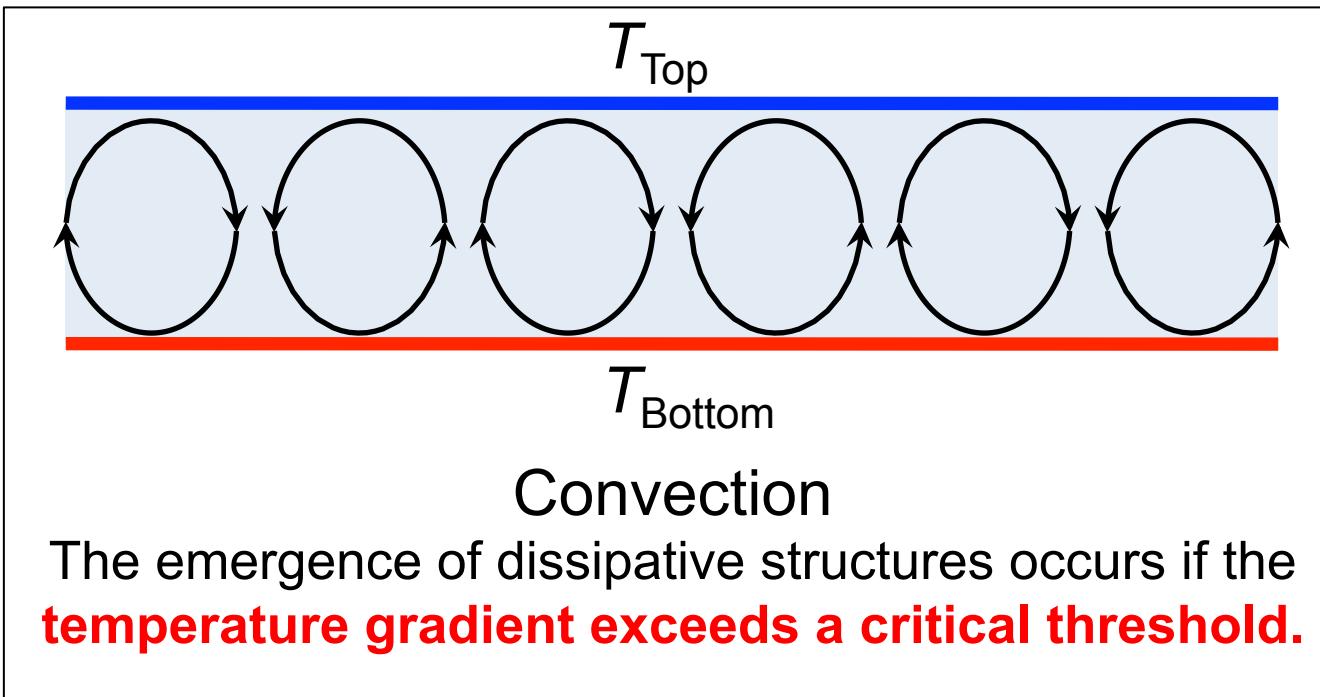
Thermodynamic disequilibrium

- Thermodynamically unstable metabolites can be formed by coupling their formation with the dissipation of the disequilibrium.



- Is it sufficient ? What does “a thermodynamic disequilibrium” really mean in the context of the origin of life?

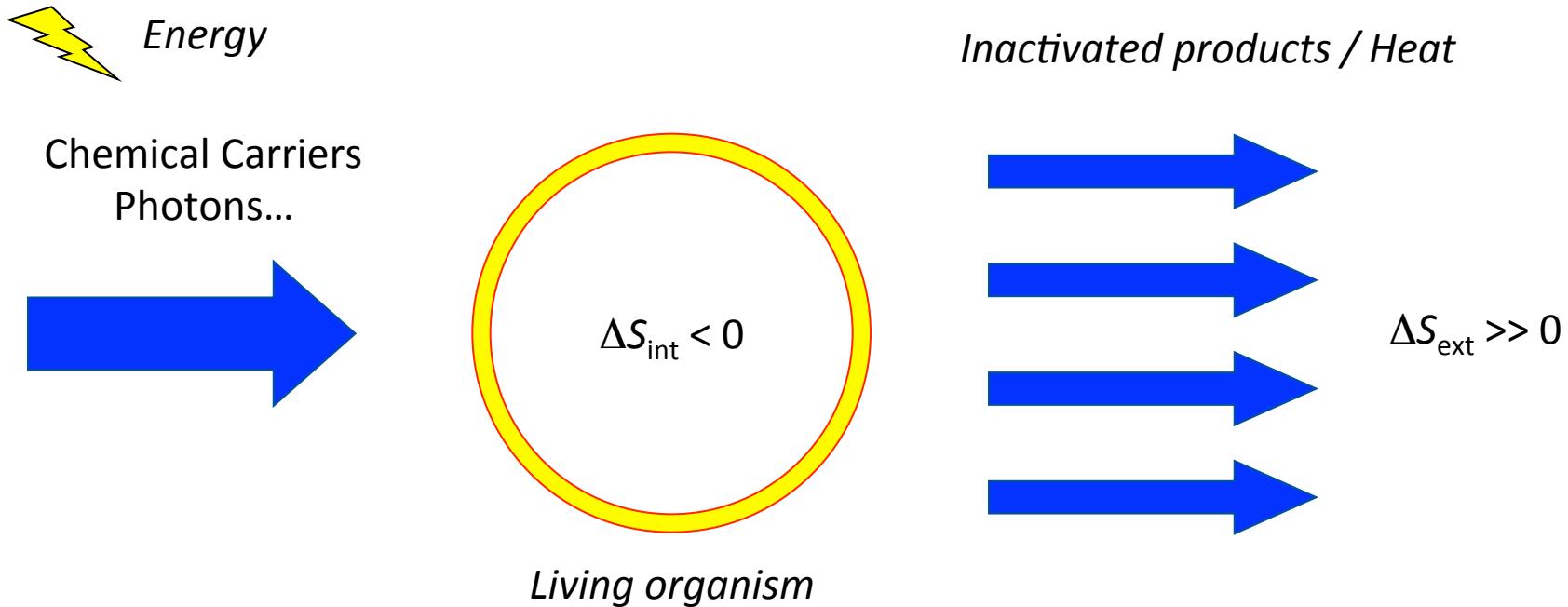
Rayleigh-Bénard instability



A similar threshold needed for the emergence of life!

Making the formation of metabolites thermodynamically favourable is not a sufficient prerequisite for the emergence of life.

Thermodynamics of self-organization in biological systems



A violation of the 2nd Law can be avoided.

How the presence of liquid water, organic matter, and free energy potentials can combine to allow for the origin of life

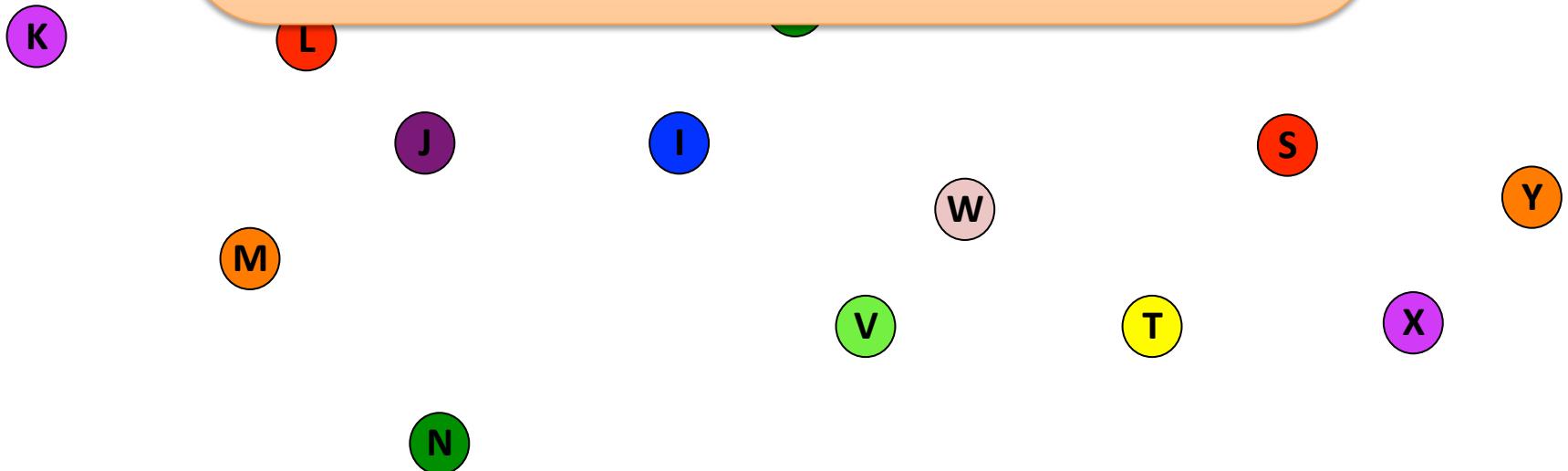
Prebiotic chemistry

The origin of life: finding the good combination

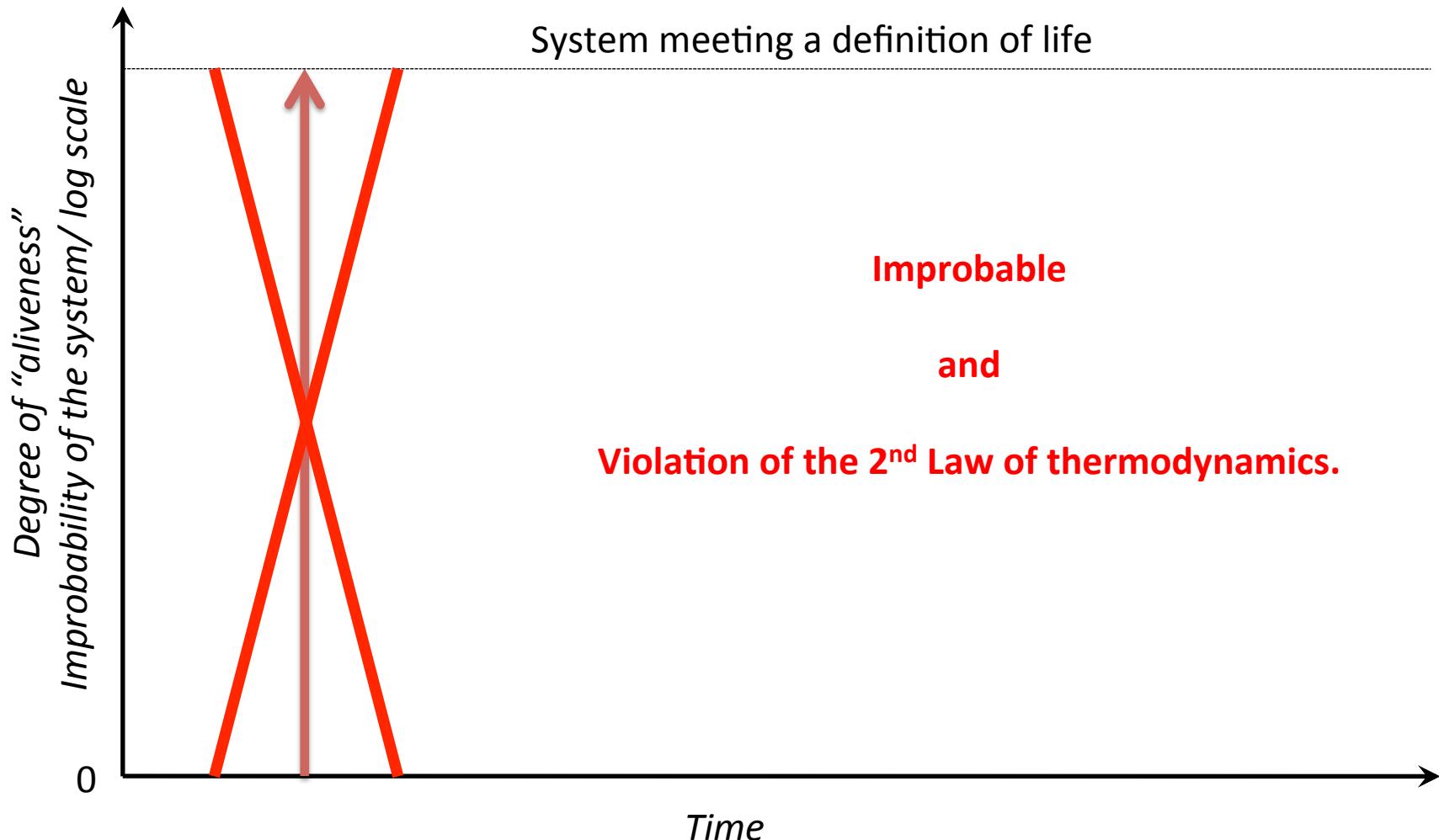
Probability of the spontaneous formation of a bacteria from its components:

1 / $10^{100\ 000\ 000\ 000}$

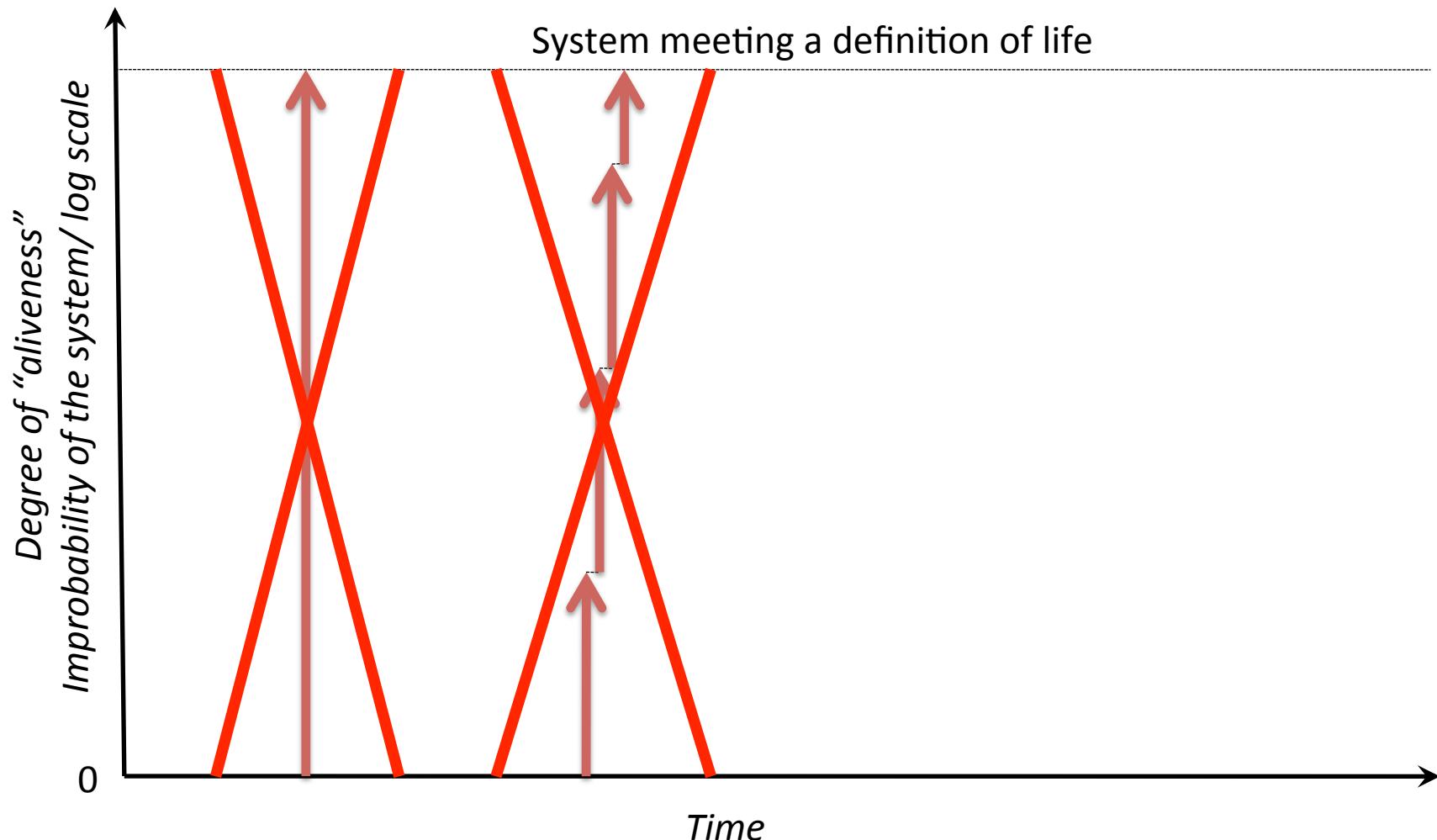
Beginnings of cellular life, H. J. Morowitz, 1992



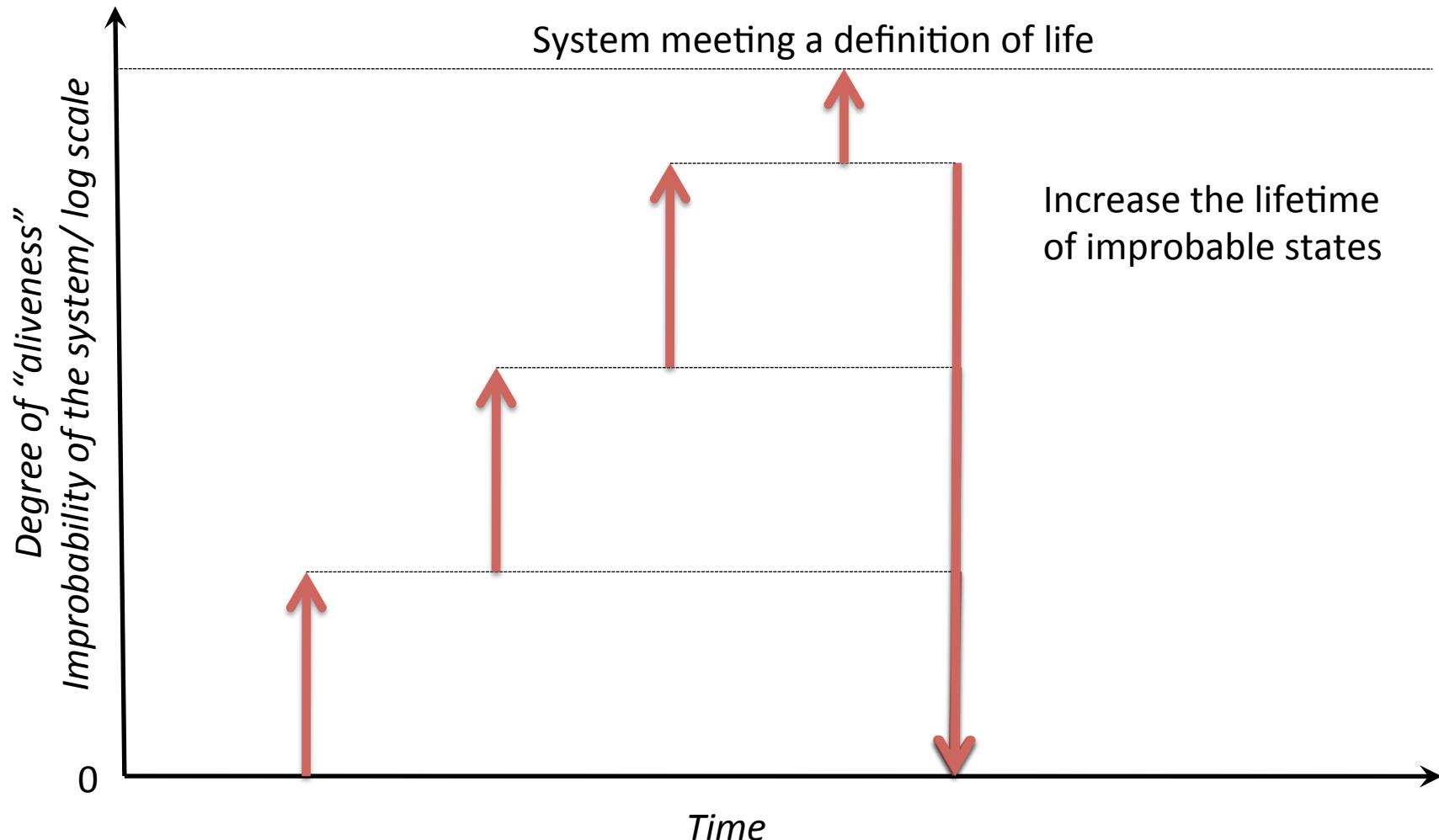
The result of a “happy accident”



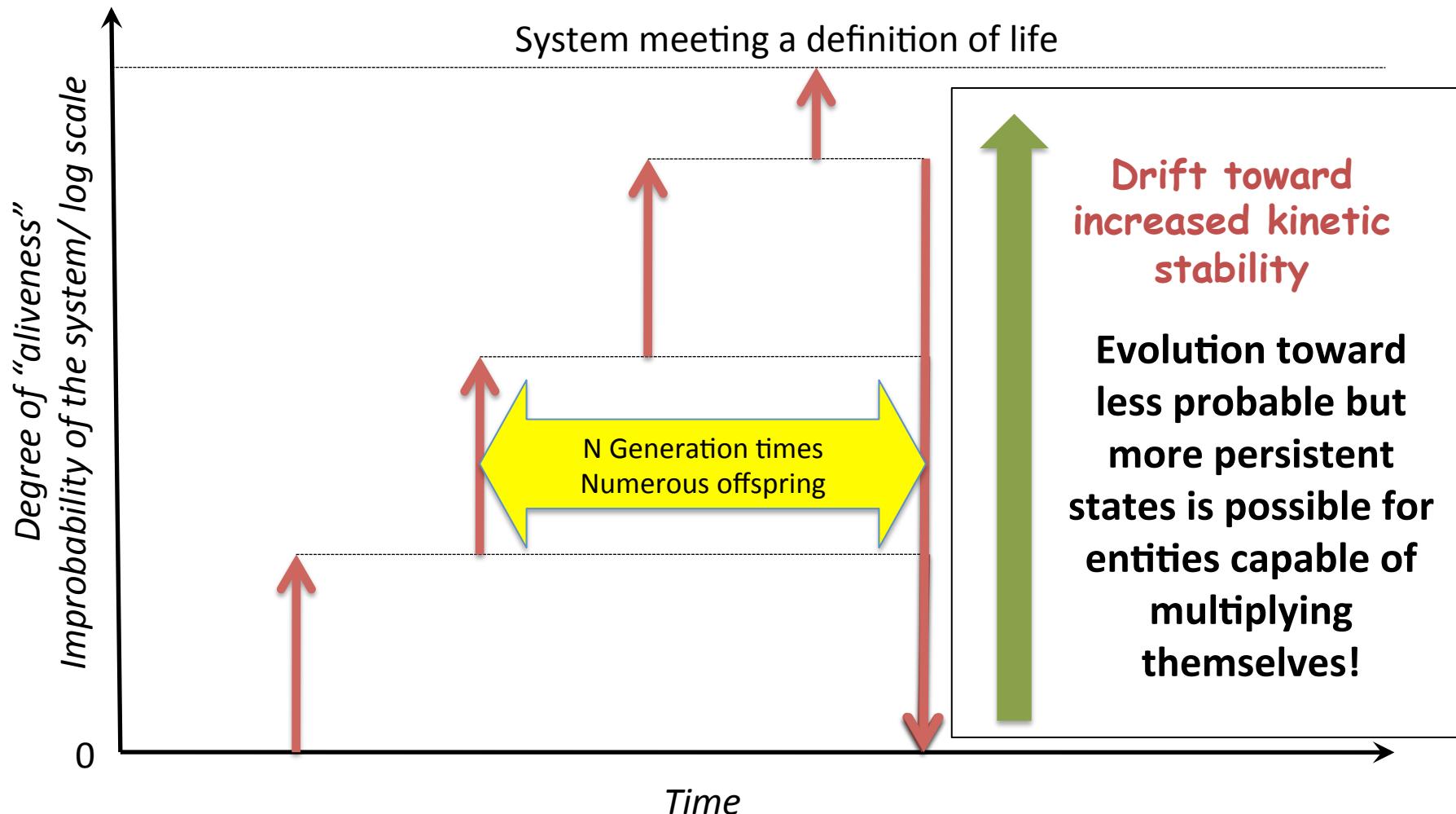
A gradual transition through unstable improbable states



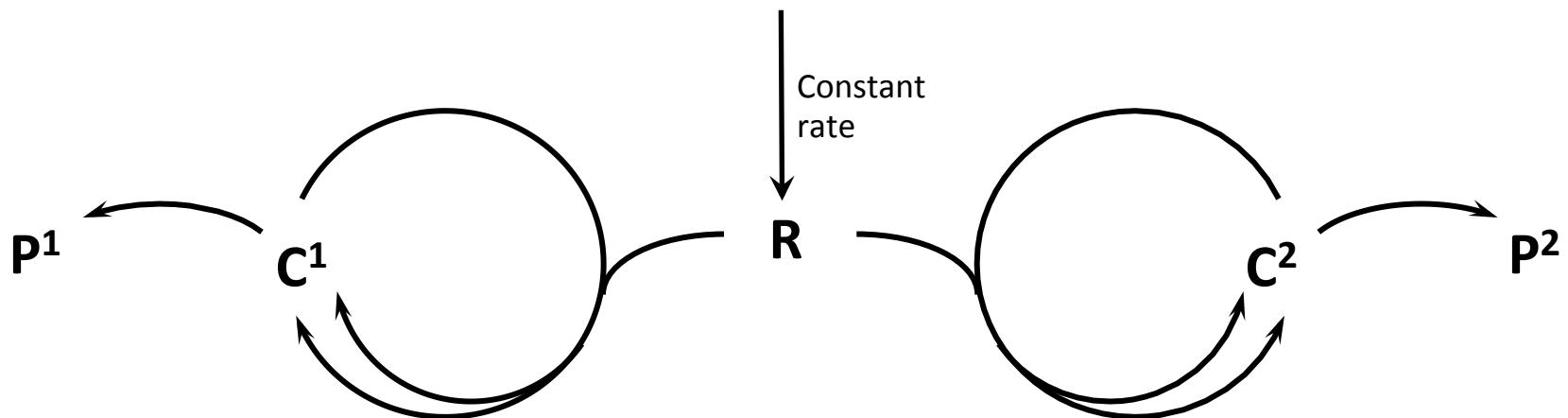
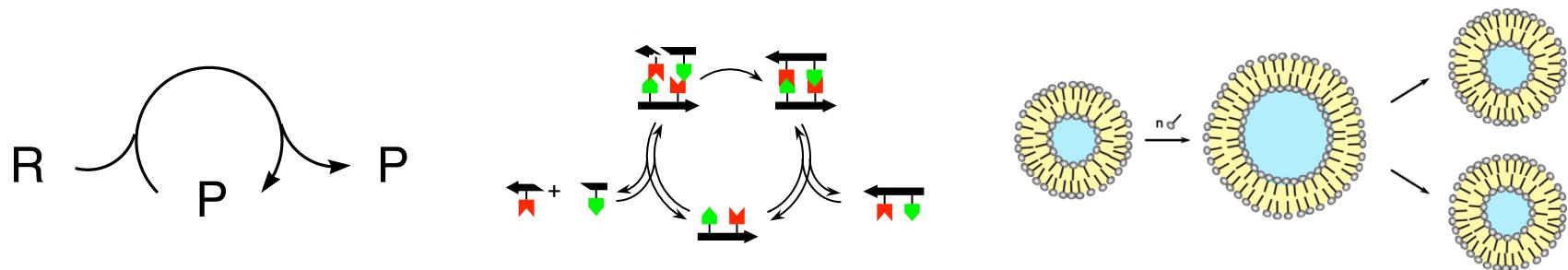
A gradual transition through “stable” improbable states



Is there a mean of increasing time stability without changing thermodynamic stability?



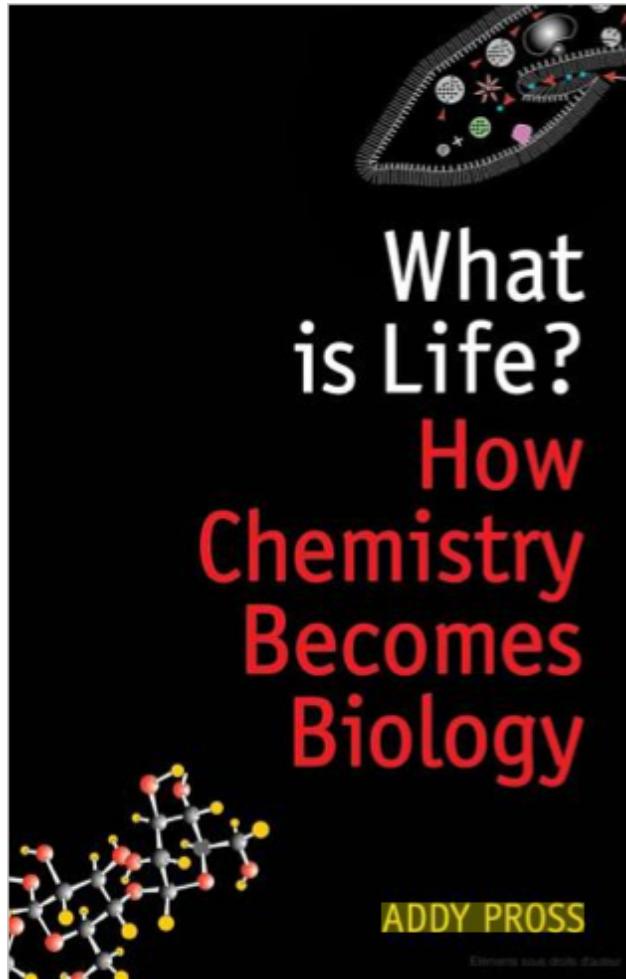
Autocatalysis and Replication



$$[C^1] = 0 \text{ or } [C^2] = 0$$

S. Lifson *J. Mol. Evol.* 1997, 44, 1-8

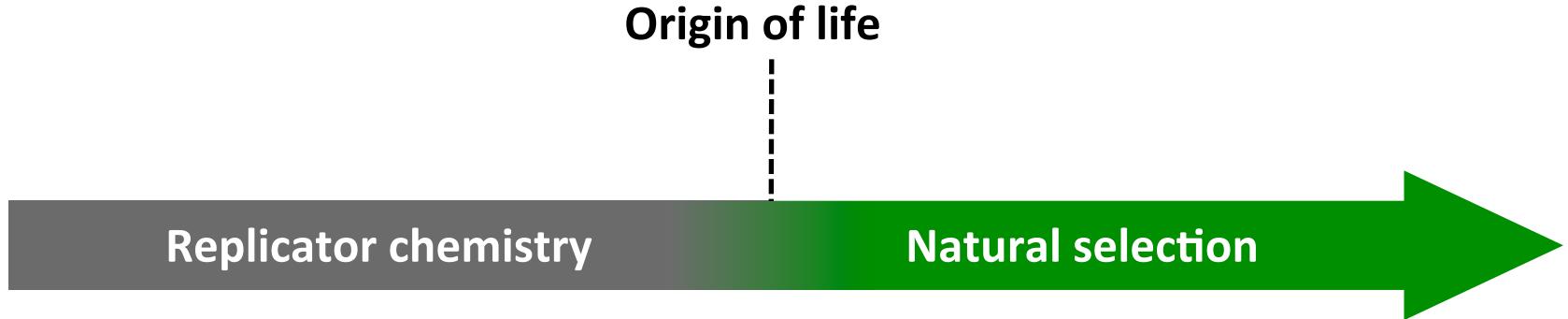
Dynamic kinetic stability



- A kind of stability that is specific to processes of reproduction
 - ✓ Replication
 - ✓ Autocatalysis

A. Pross *J. Syst. Chem.* **2012**, 58, 465

Chemical and biological evolution



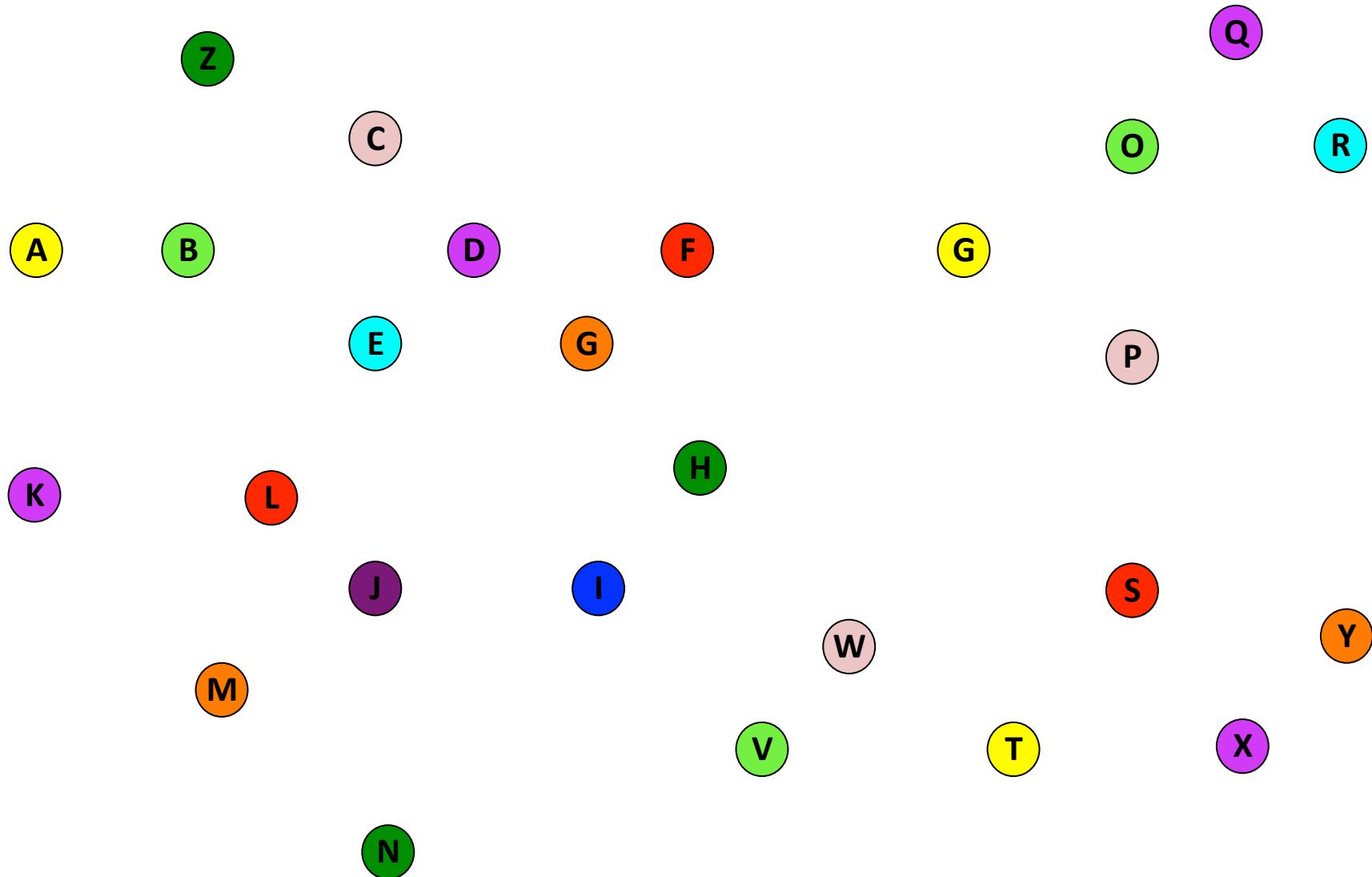
- **Driving force = Dynamic Kinetic Stability**

A. Pross *J. Syst. Chem.* **2011**, 2:1

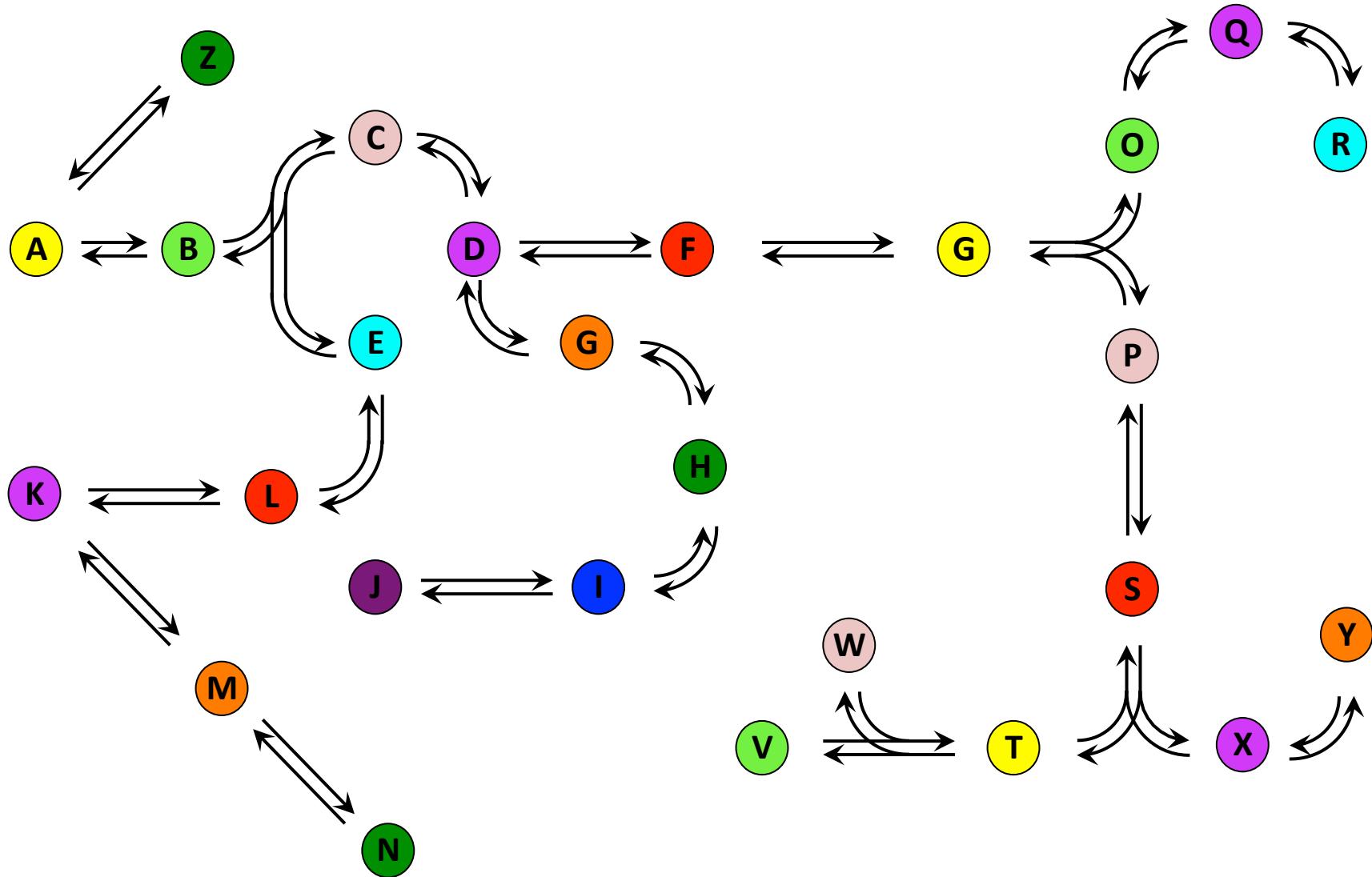
- **Persistence (time stability) more general than thermodynamic stability**

R. Pascal, A. Pross *Chem. Commun.* **2015**; DOI:10.1039/C5CC06260H

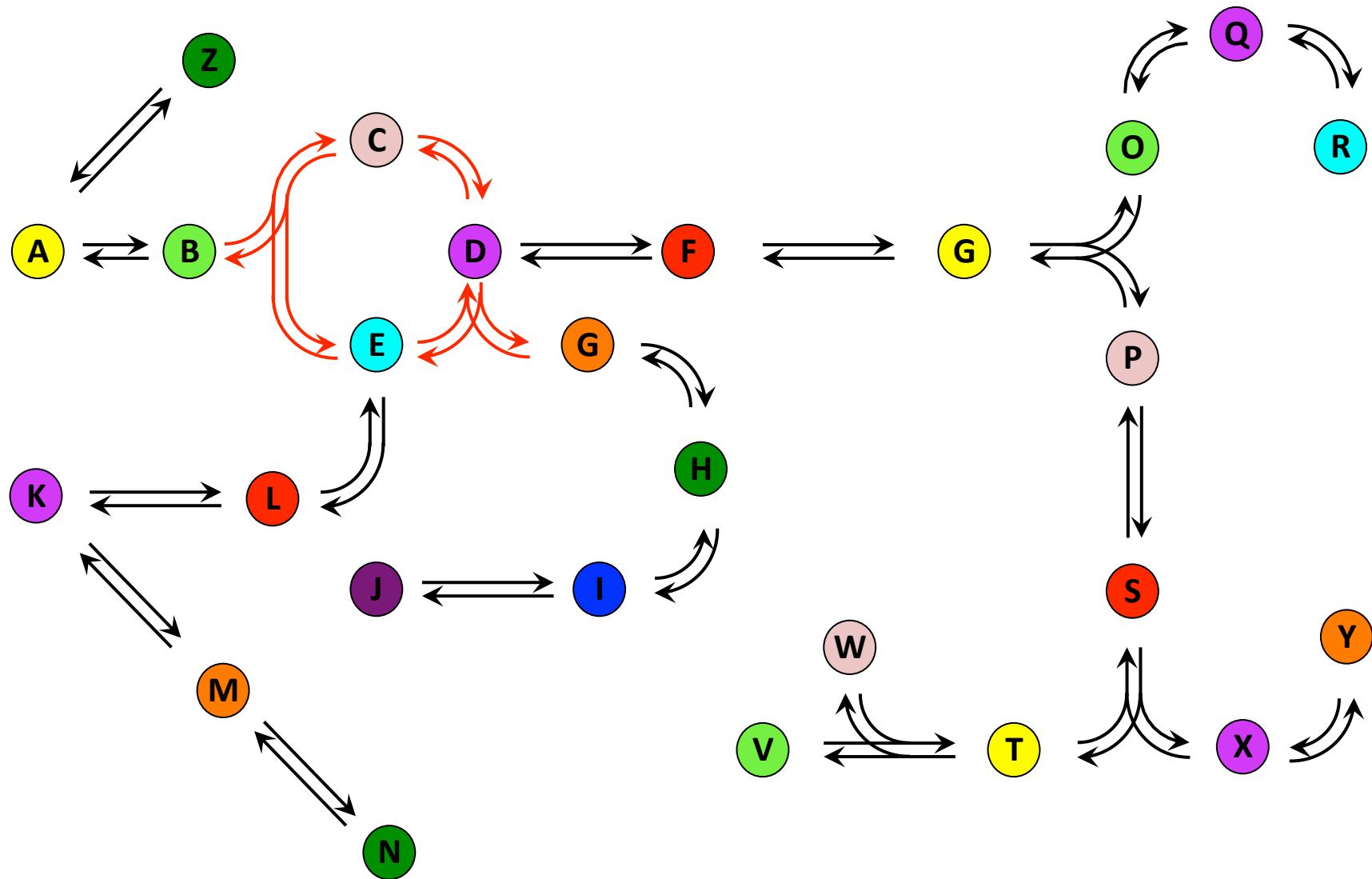
Systems view



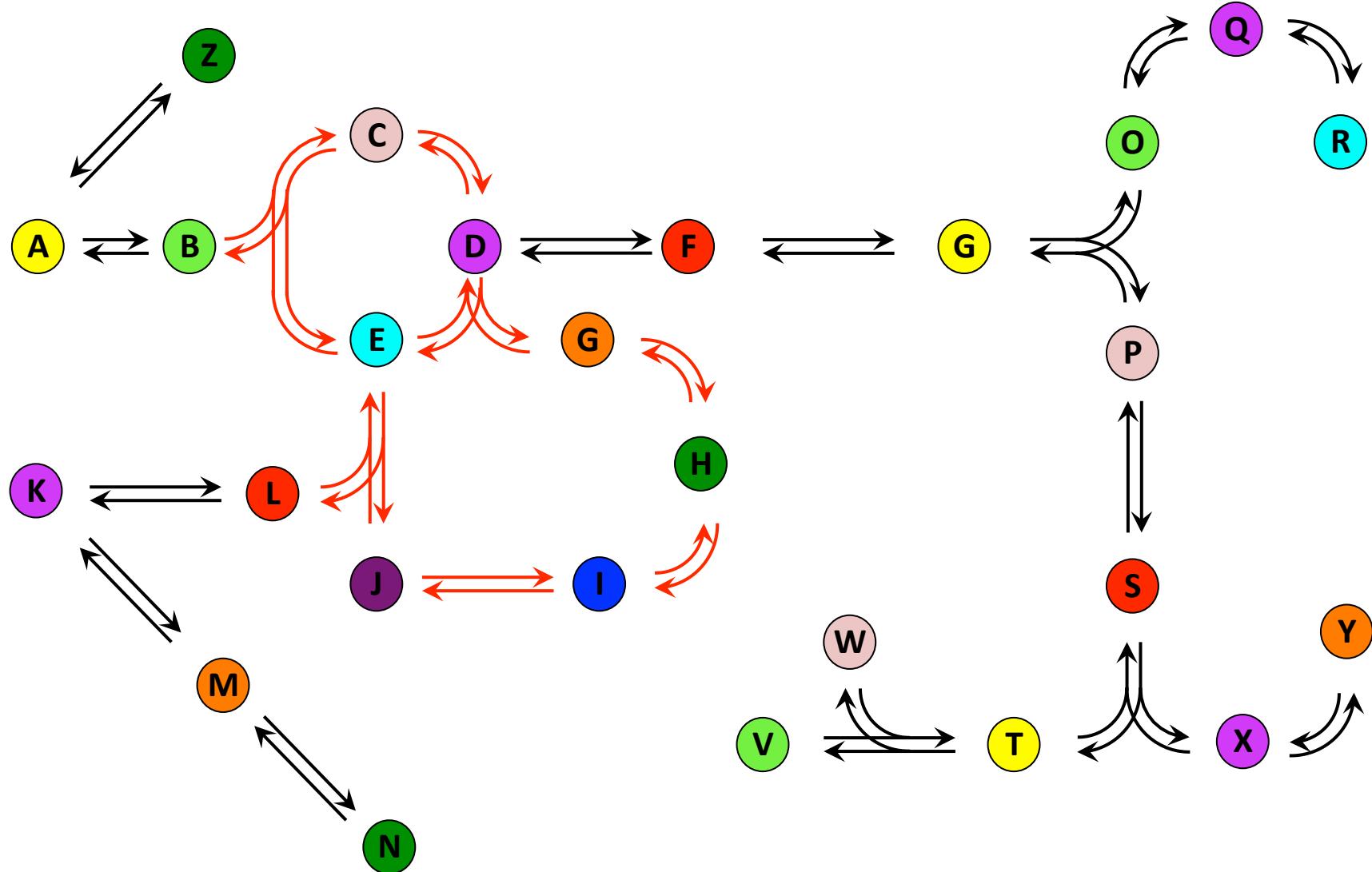
Systems view



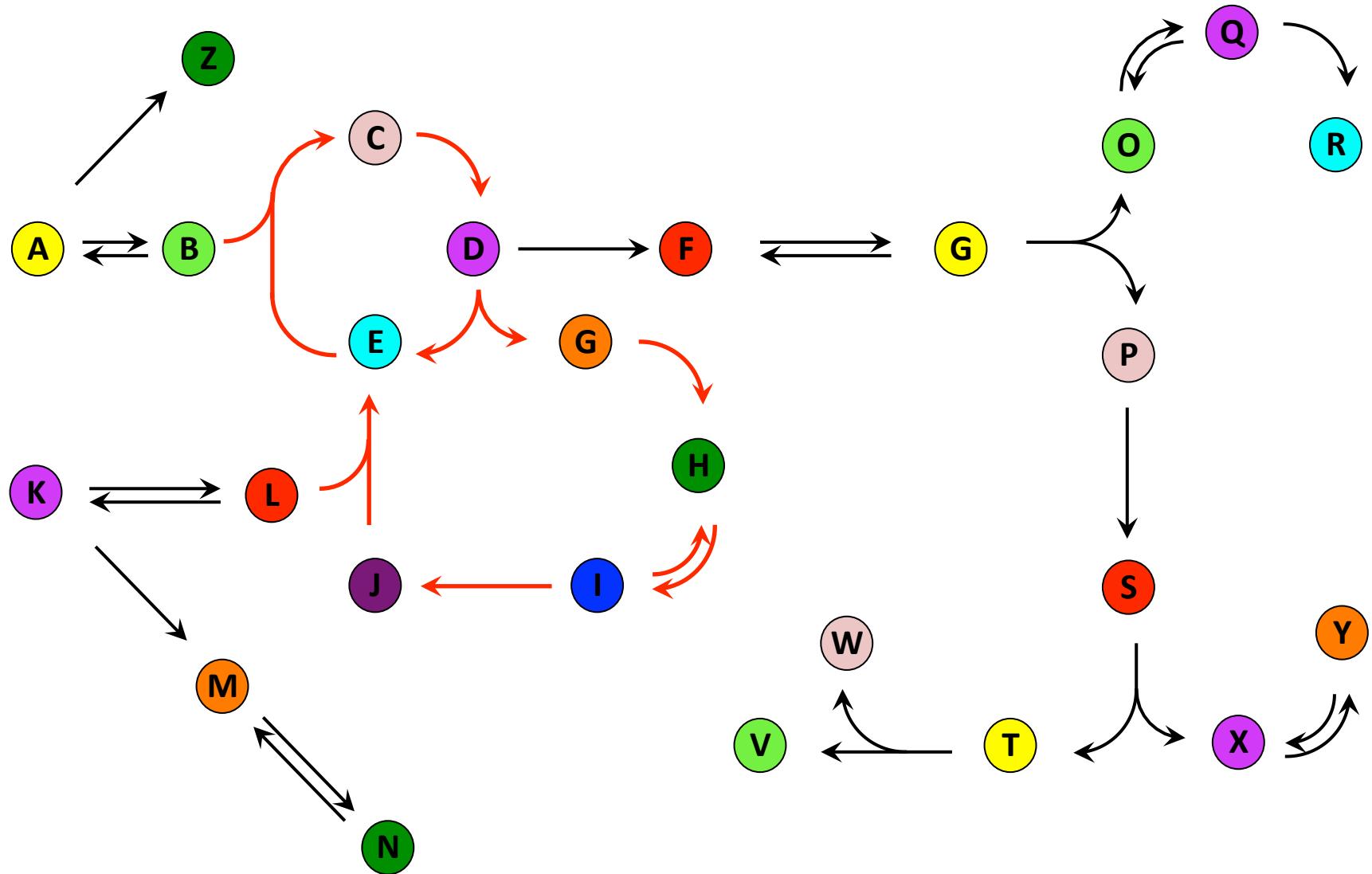
Catalytic Cycles



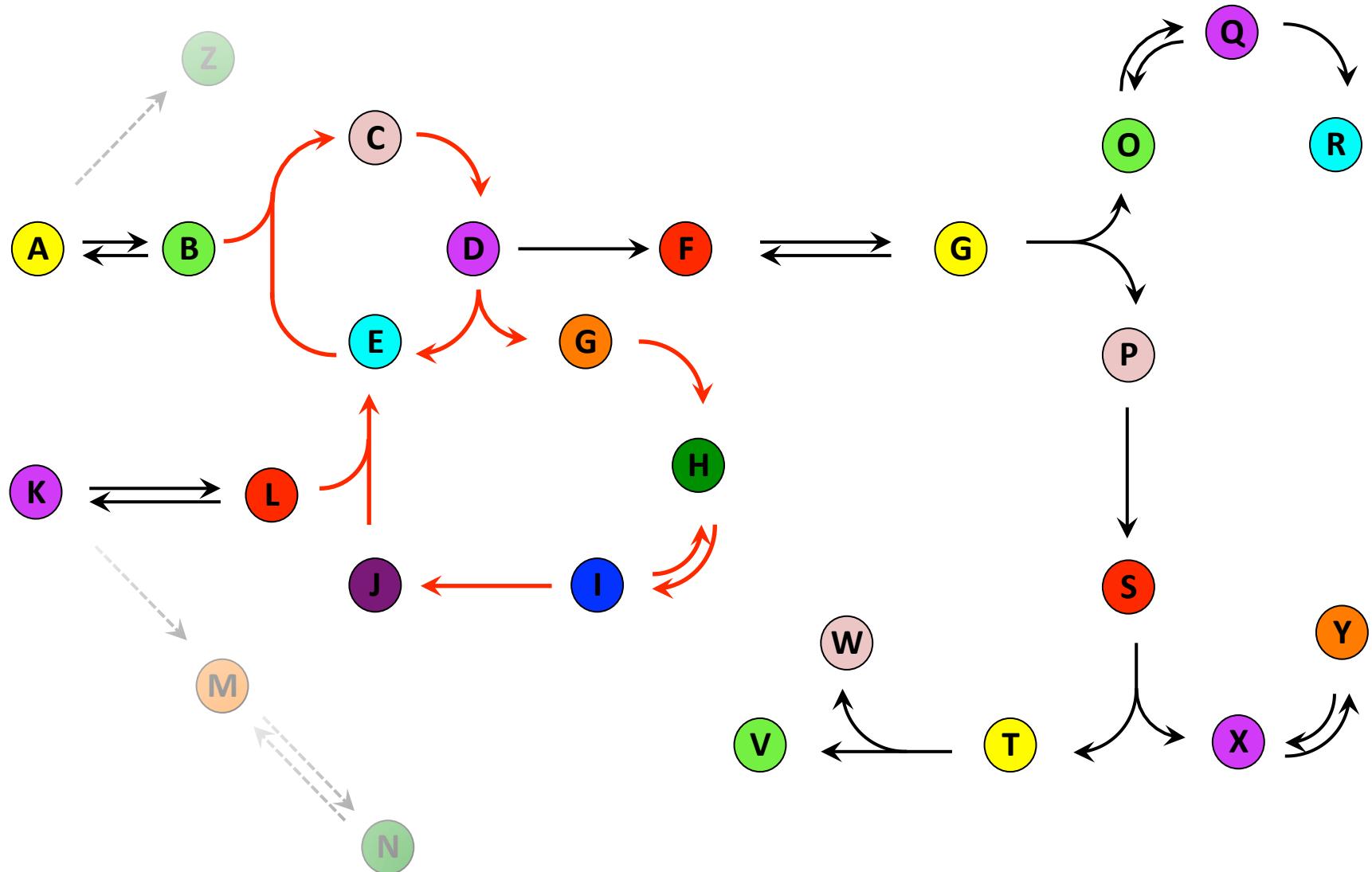
Autocatalysis



Far from equilibrium

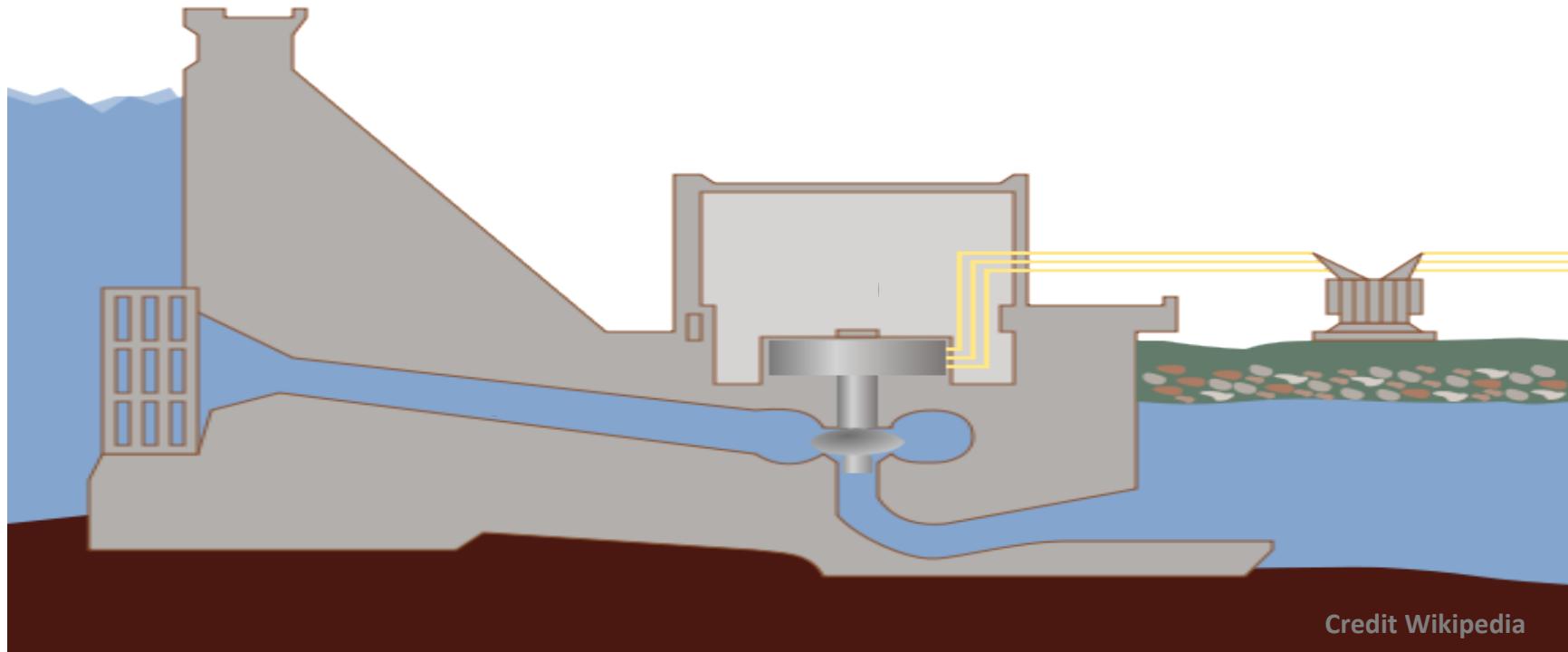


Kinetic selection

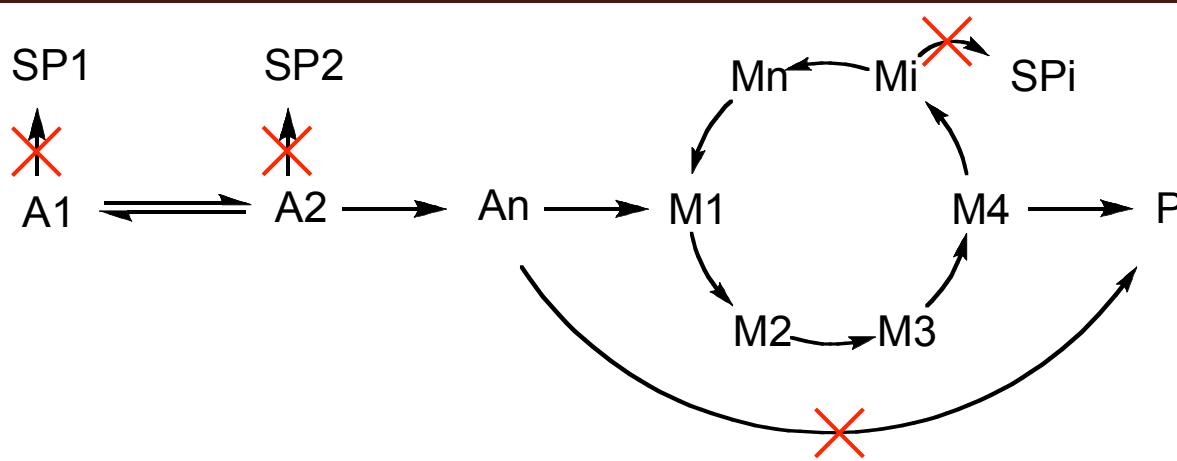


"The development of a metabolism requires species to be held far from equilibrium by kinetic barriers"

A. Eschenmoser, *Orig. Life Evol. Biosph.* **1994**, 24, 389; *Angew. Chem. Int. Ed.* **2011**, 50, 12412.

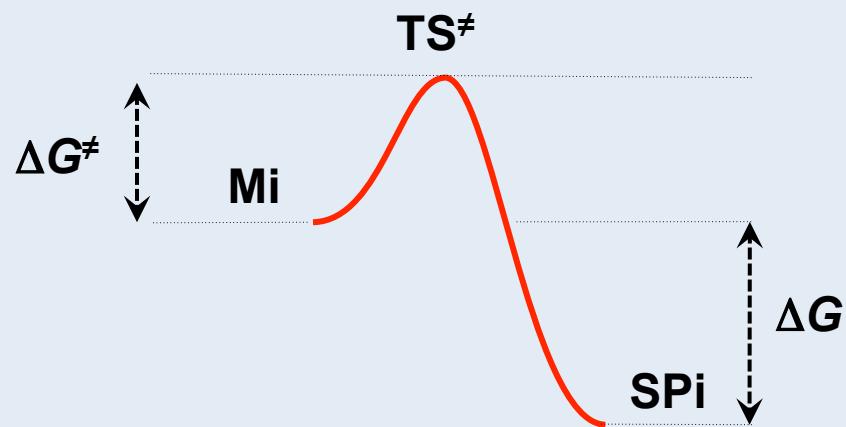


Credit Wikipedia



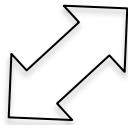
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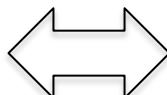


$$k = \kappa \frac{k_B T}{h} e^{-(\Delta G^\ddagger / RT)}$$

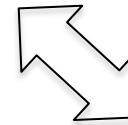
Lifetime of the system
 $k, t_{1/2}$



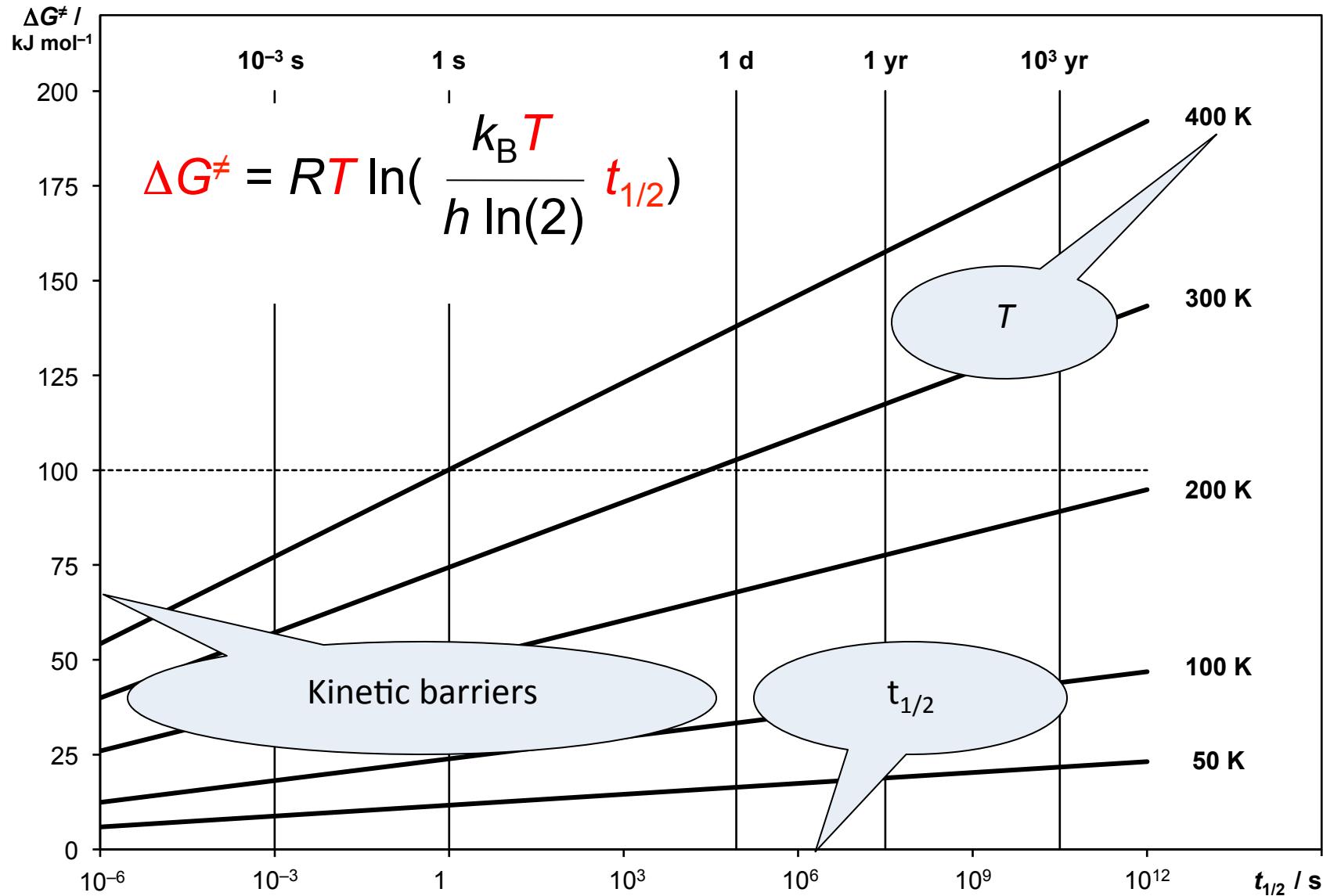
Temperature
 T



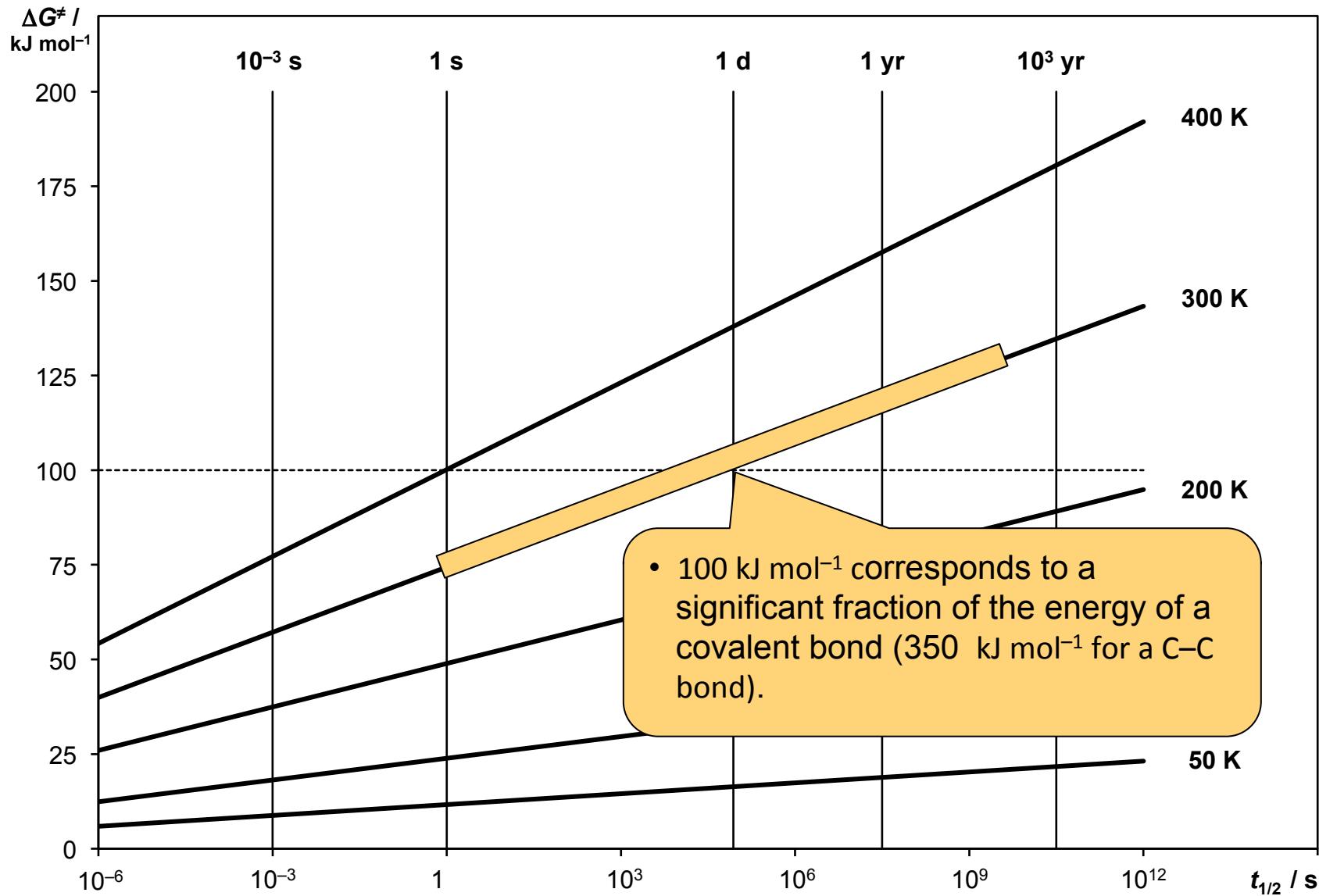
Kinetic barriers
 ΔG^\ddagger



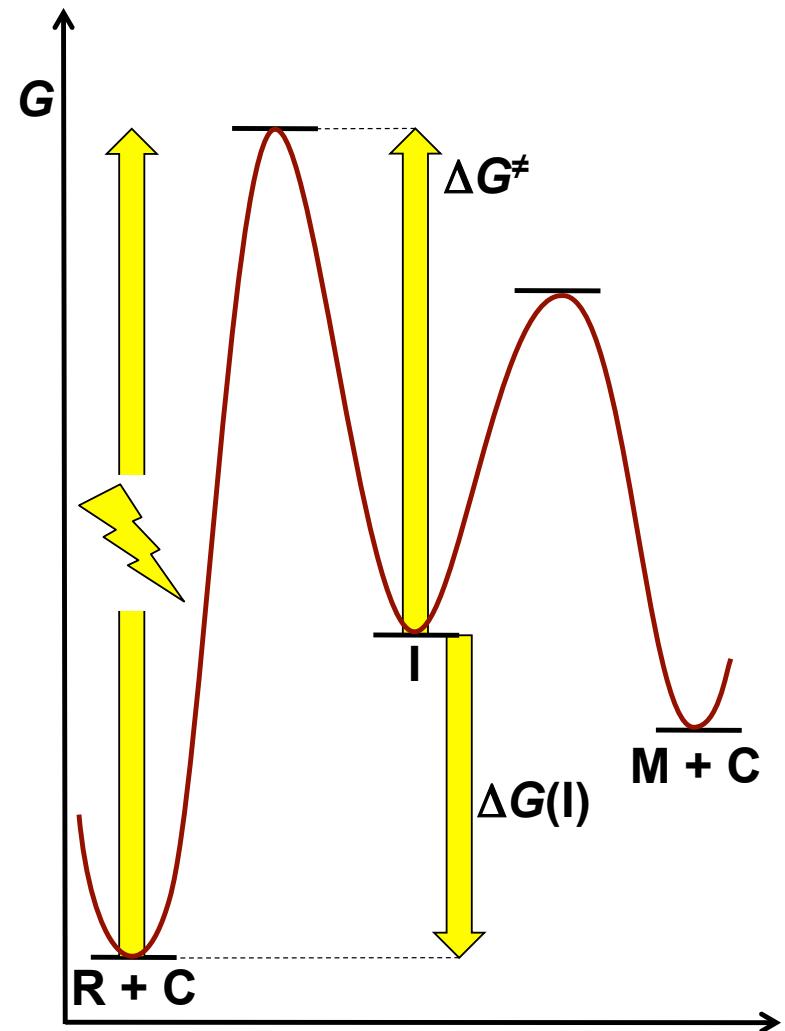
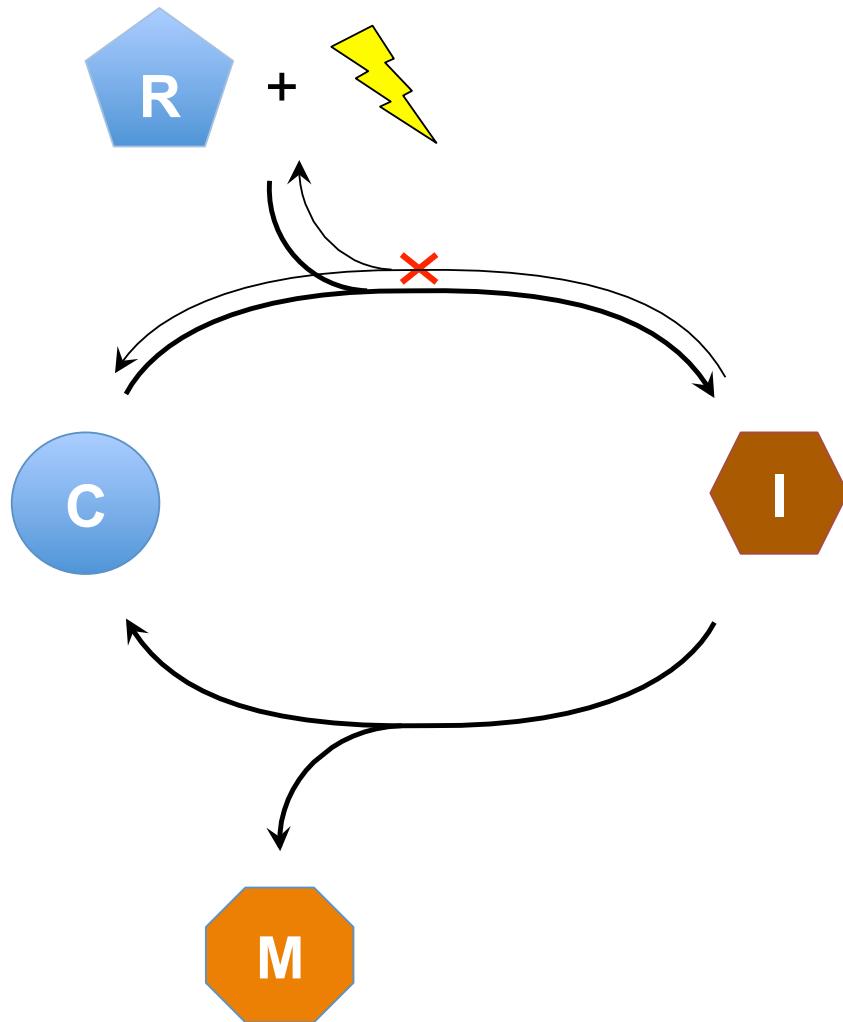
Graphical representation



At 300 K $\Delta G^\ddagger \sim 100 \text{ kJ mol}^{-1}$

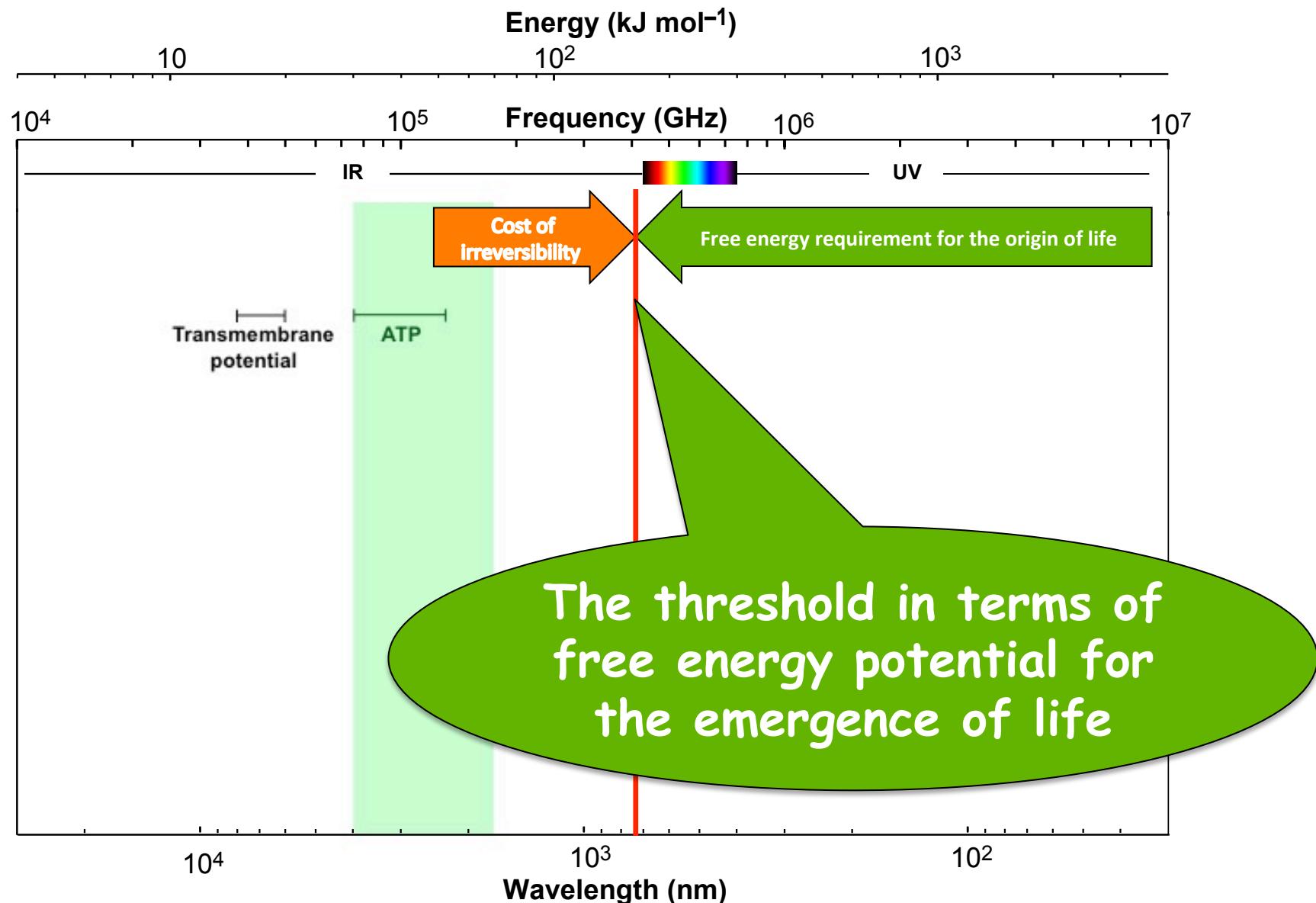


The energetic cost of kinetic irreversibility



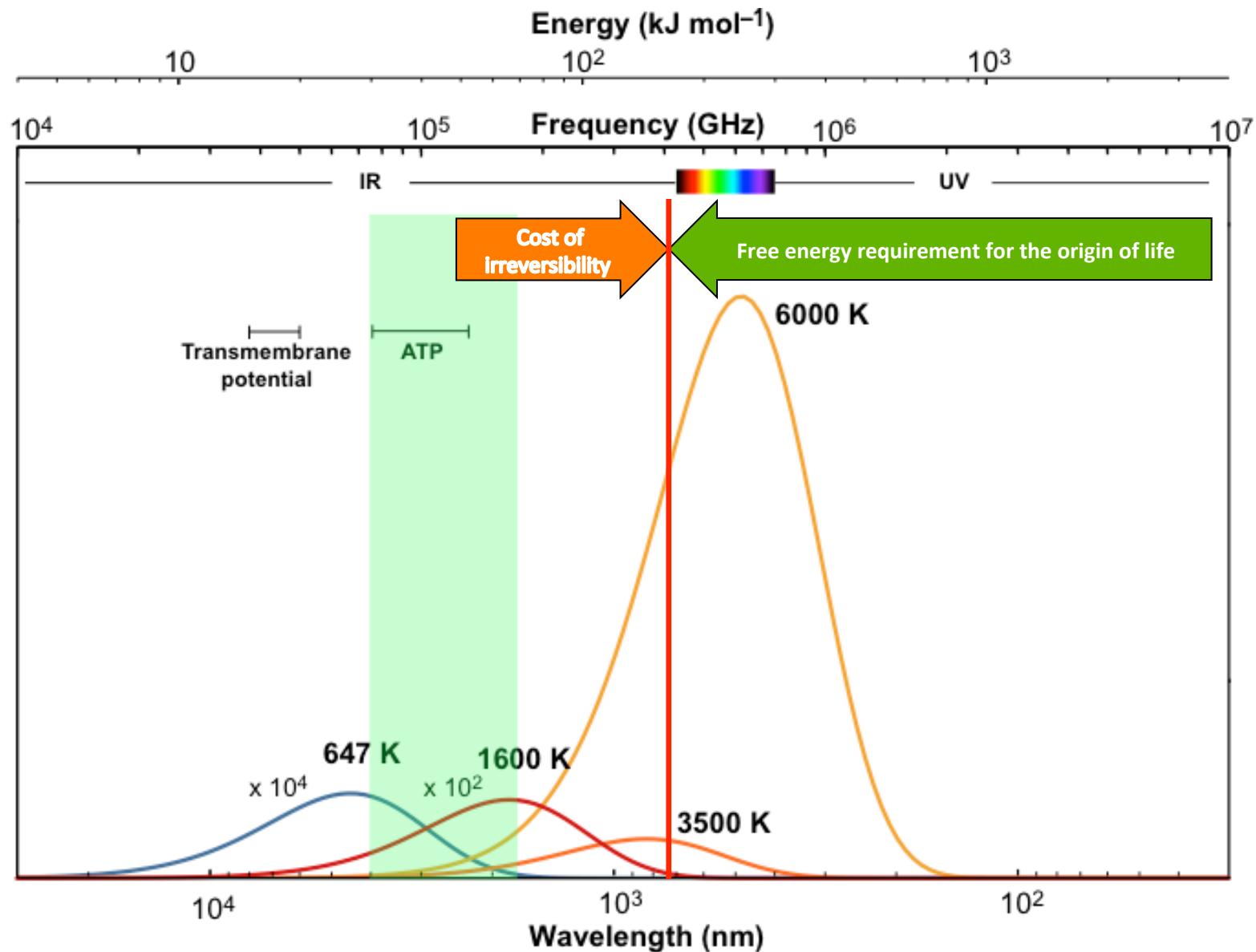
Only part of the free energy is available for self-organization.

The need of energy for sustaining life and its origin



Adapted from Lineweaver and Chopra, *Ann. Rev. Earth Planet. Sci.* **2012**, 40, 597-623

The need of energy for sustaining life and its origin

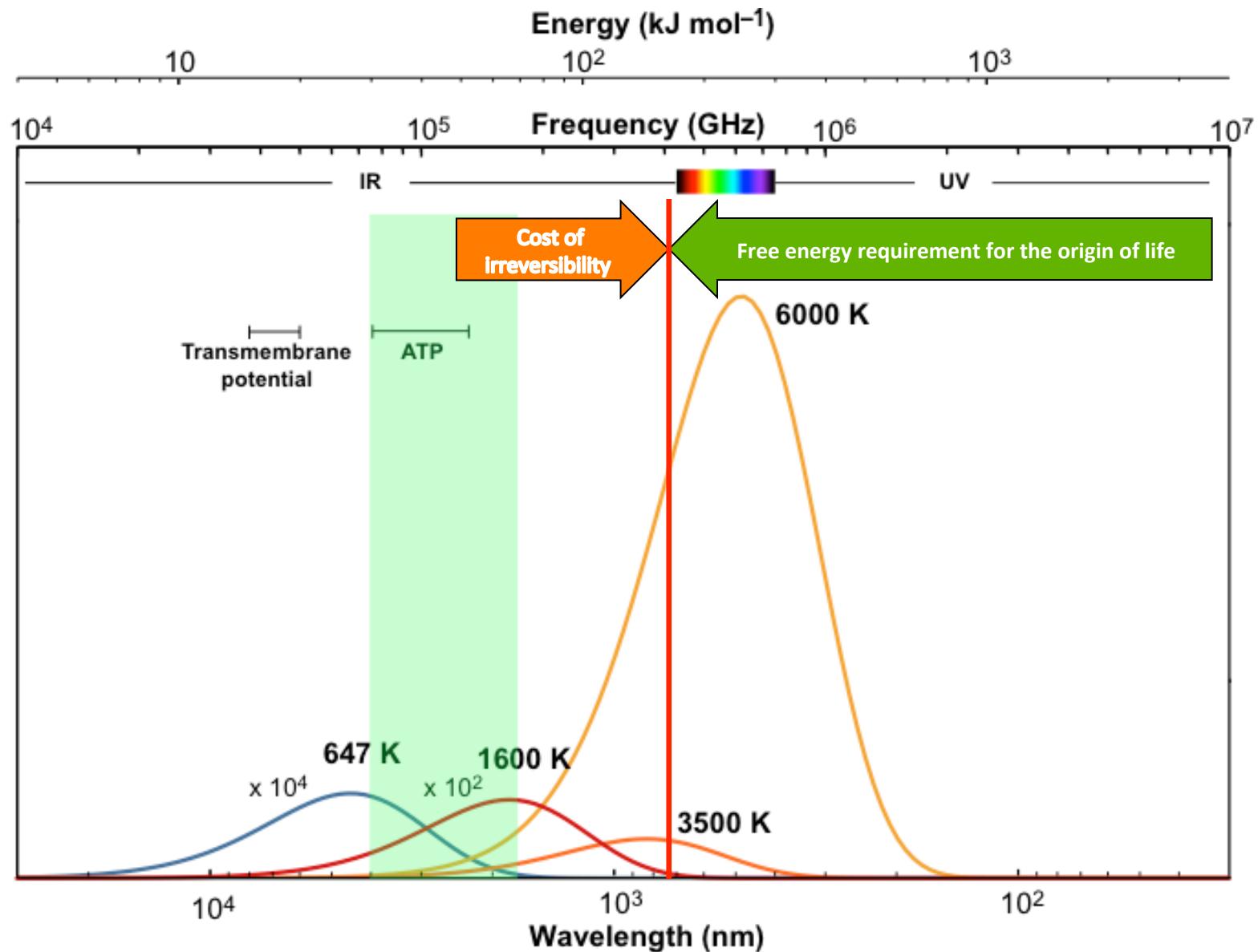


How far from equilibrium must a system be to undergo a transition towards life?

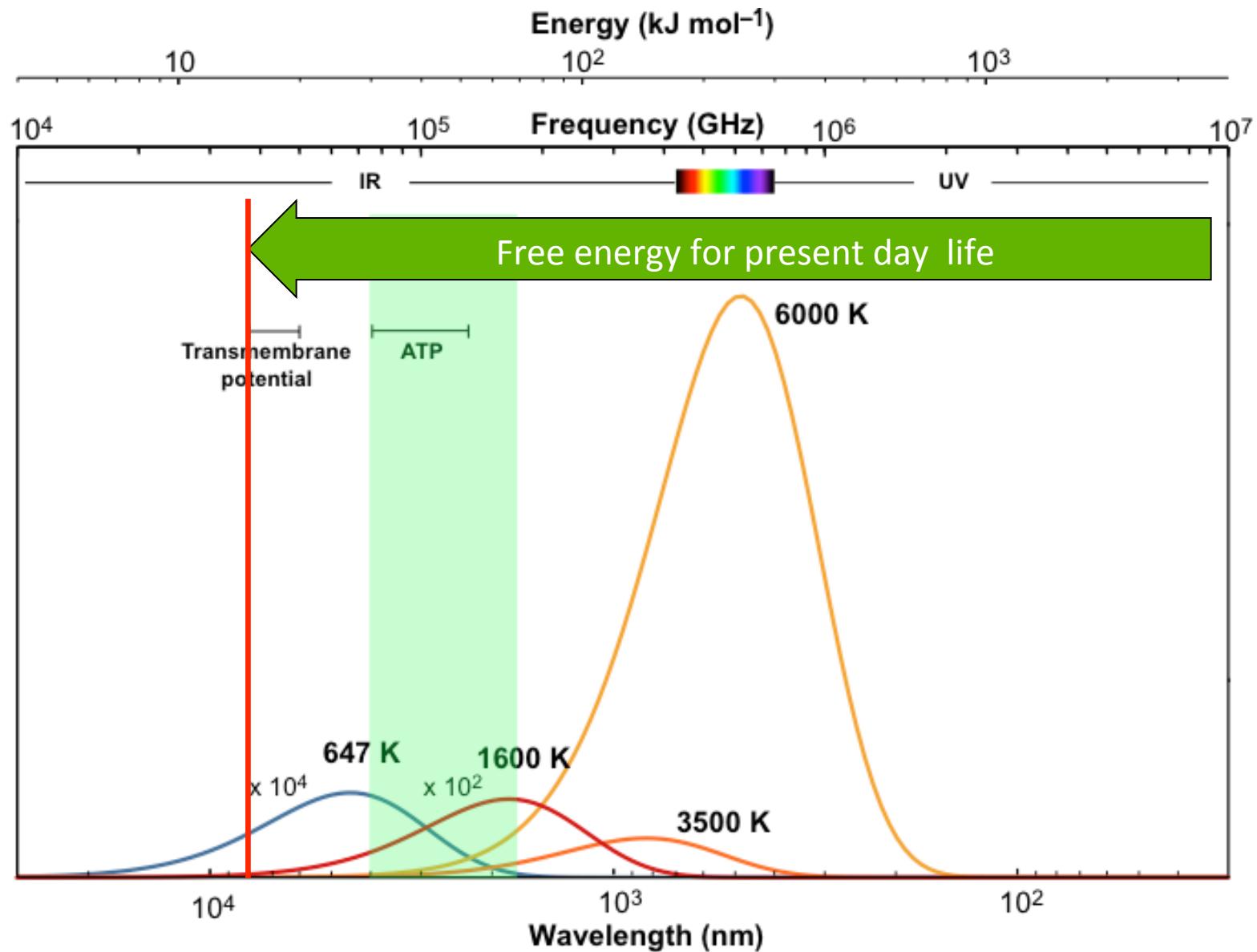
The winning combination:

- Temperature as low as possible but compatible with liquid water: c.a. 300 K
- Covalent bonds (ensuring kinetic barriers compatible with the generation time of the self-reproducing system)
- Free energy available with a potential equivalent to that of visible light

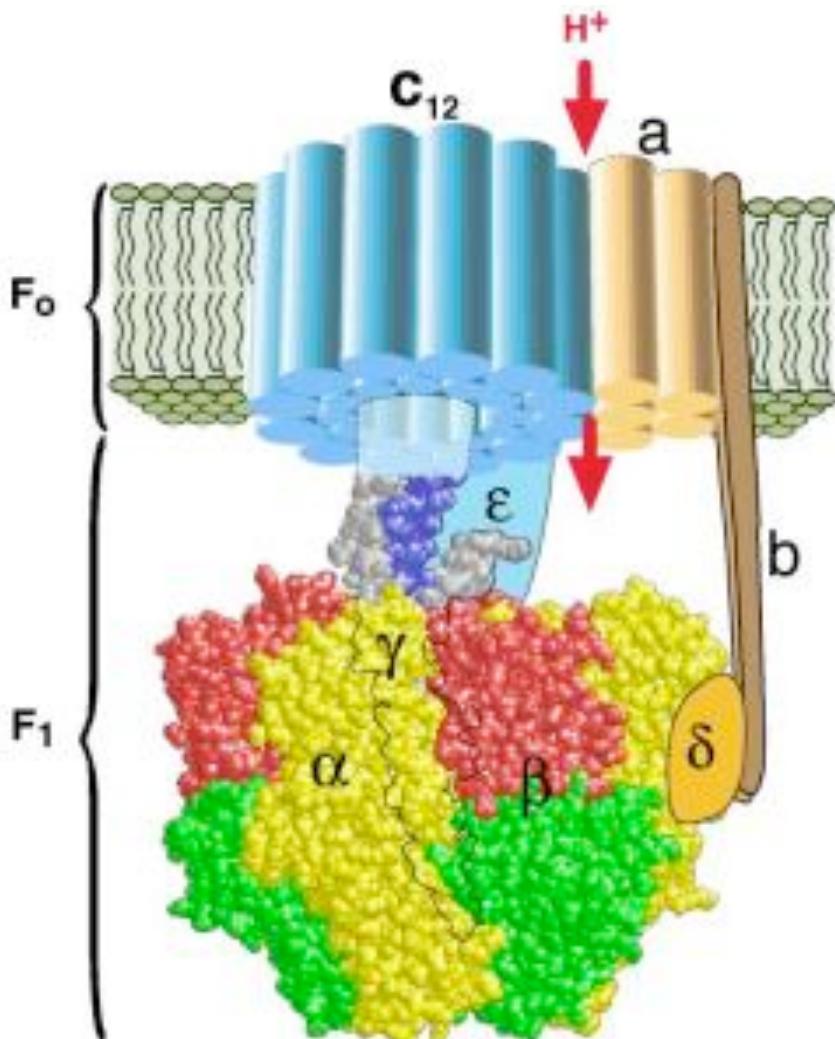
The need of energy for sustaining life and its origin



The need of energy for sustaining life and its origin



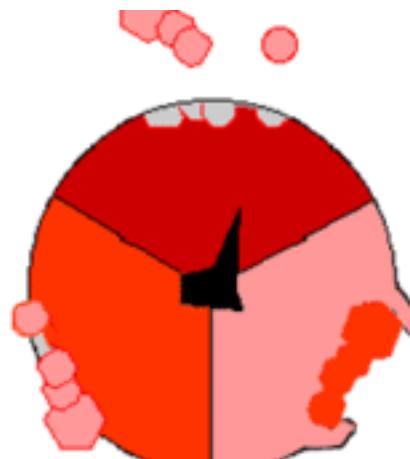
ATPase: the proton pump



H. Wang and G. Oster (1998). Nature 396:279-282.

A complex molecular machine is needed to convert the potential energy of proton gradient across the membrane into ATP.

ATPase (proton pump) couples the translocation of several protons across the membrane to the synthesis of an ATP molecule.



Icy moons

No simple possibility for the emergence of life in the deep ocean of icy moons

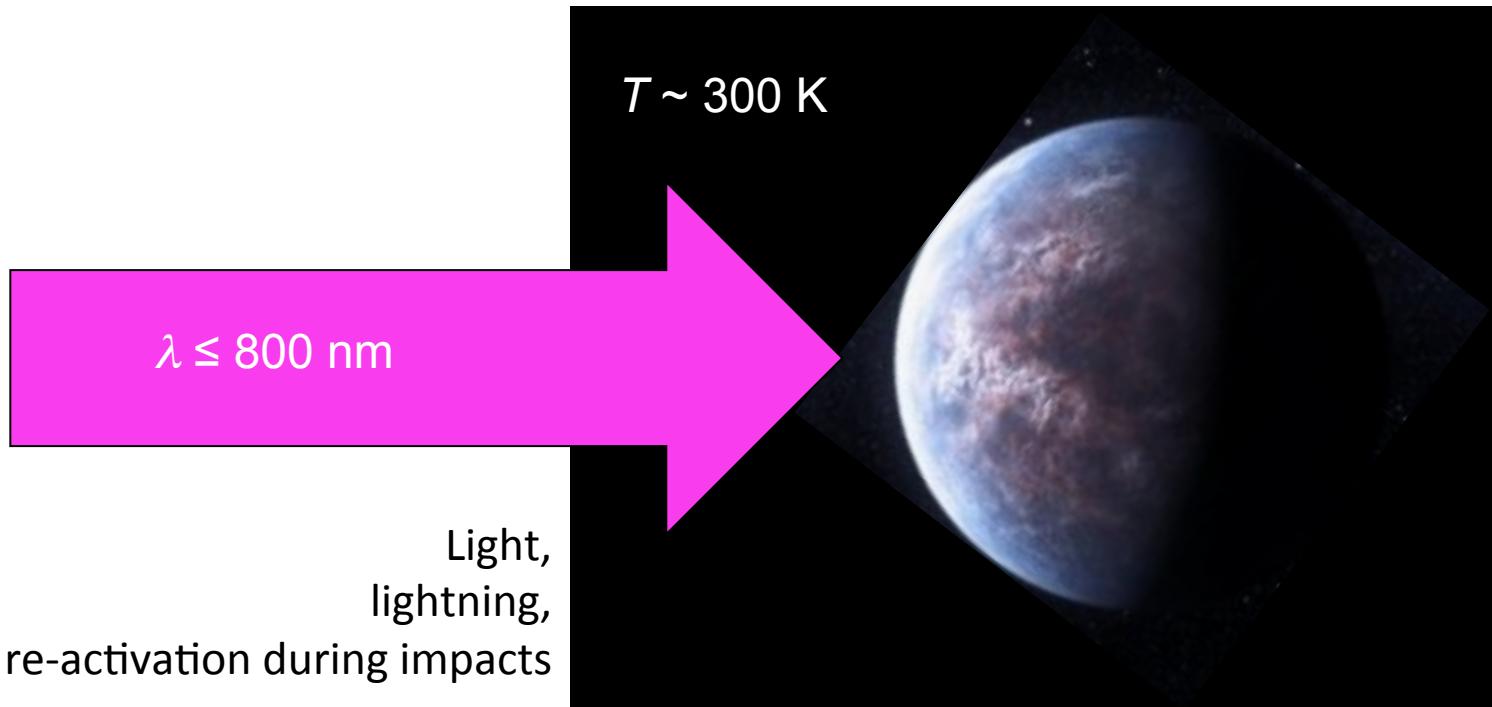
- ✓ Presence of water
- ✓ Temperatures allowing water to be present in the liquid state
- ✓ Organic matter
- ✗ Free energy potential equivalent to that of visible light

No easily available driving force.
The emergence of life would only rely on the occurrence of unlikely events

The habitability of icy moons

- No driving force for the emergence of life.
- The origin of life in the absence of process allowing the selection of efficient self-reproducing systems is extremely improbable.
- The presence of life would only rely on the highly speculative possibility of panspermia.

Favourable habitat for the origin of life





- The DSBC group of the IBMM
 - Dr. L. Boiteau
 - Dr. Z. Liu
 - Dr. J.-C. Rossi
 - D. Beaufils
 - G. Ajram
- Collaborations
 - Dr. G. Danger (University of Marseille)
 - Prof. J. D. Sutherland (MRC-LMB, Cambridge)
 - Prof. A. Pross (Ben Gurion University of the Neguev)
- COST CM1304
- Agence Nationale de la Recherche ANR PeptiSystems (2014-2018)
- SIMONS FOUNDATION



Emergence and Evolution of
Complex Chemical Systems

