

Thermodynamic Probability and Reaction Kinetics in Prebiotic Systems

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Abstract

This paper models the thermodynamic and kinetic feasibility of prebiotic chemical reactions by connecting entropy change, Gibbs free energy, and microstate probability. The framework provides a quantitative link between molecular reaction rates and statistical thermodynamics, enabling estimation of the likelihood of complex molecule formation under early Earth conditions.

1 Introduction

Abiogenesis can be approached as a statistical thermodynamic process [Eigen, 1971, Smith and Lee, 2021] , where the formation of complex molecules depends on both the microstate probability and the energy landscape of the surrounding medium. The present work formulates this connection using entropy, Gibbs free energy, and reaction-rate theory [Atkins and de Paula, 2010].

2 Methods

2.1 Thermodynamic Foundation

The statistical behavior of prebiotic chemical systems was modeled by relating entropy change (ΔS) to the ratio of accessible microstates before and after a reaction:

$$\Delta S = k_B \ln \left(\frac{\Omega_f}{\Omega_i} \right), \quad (1)$$

where Ω_i and Ω_f represent the number of accessible microstates in the initial and final states, respectively. A negative ΔS corresponds to an ordering process—consistent with the thermodynamic cost of molecular self-organization.

2.2 Gibbs Energy and Reaction Directionality

The thermodynamic feasibility of each reaction was expressed as:

$$\Delta G = \Delta H - T\Delta S, \quad (2)$$

and the relative probability of the forward and reverse processes follows the Boltzmann relation:

$$\frac{P_{\text{forward}}}{P_{\text{reverse}}} = \exp \left(-\frac{\Delta G}{RT} \right). \quad (3)$$

2.3 Reaction Probability and Kinetic Scaling

The per-collision probability of reaction was defined as:

$$P_{\text{react}} = \frac{k_{\text{actual}}}{k_{\max}}, \quad (4)$$

where k_{\max} is the diffusion-limited maximum rate constant (1×10^9 to $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). From transition-state theory [Atkins and de Paula, 2010],

$$k_{\text{actual}} = \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right), \quad (5)$$

$$P_{\text{react}} = C \exp\left(-\frac{\Delta G^\ddagger}{RT}\right), \quad C = \frac{\kappa k_B T}{h k_{\max}}. \quad (6)$$

This expresses the fraction of collisions that overcome the activation barrier.

2.4 Computational and Analytical Implementation

All thermodynamic quantities were evaluated symbolically using macroscopic variables ($\Delta H, T, k_{\max}$) and estimated molecular parameters (ΔG^\ddagger , diffusion coefficients). The framework can be extended to multi-step prebiotic reaction networks to obtain probability distributions of feasible reaction pathways.

2.5 Numerical Illustration

To demonstrate consistency between thermodynamic, kinetic, and activation–energy formulations, three representative examples were computed.

(a) From ΔH and ΔS .

$$\Delta G = \Delta H - T\Delta S, \quad (7)$$

$$P_{\text{thermo}} = \exp\left(-\frac{\Delta G}{RT}\right), \quad (8)$$

for peptide–bond formation at 298 K ($\Delta H = 21 \text{ kJ mol}^{-1}$, $\Delta S = -120 \text{ J mol}^{-1} \text{ K}^{-1}$) [Atkins and de Paula, 2010] gives $\Delta G = 56.8 \text{ kJ mol}^{-1}$ and $P_{\text{thermo}} \approx 1.1 \times 10^{-10}$.

(b) From reaction rates.

$$P_{\text{react}} = \frac{k_{\text{actual}}}{k_{\max}}, \quad (9)$$

with $k_{\text{actual}} = 10^3$ and $k_{\max} = 10^9 (\text{M}^{-1} \text{ s}^{-1})$ yields $P_{\text{react}} = 10^{-6}$.

(c) From activation free energy.

$$P_{\text{react}} = C \exp\left(-\frac{\Delta G^\ddagger}{RT}\right), \quad (10)$$

$$C = \frac{\kappa k_B T}{h k_{\max}}, \quad (11)$$

and for $\Delta G^\ddagger = 75 \text{ kJ mol}^{-1}$, $T = 298 \text{ K}$, one obtains $C = 6.2 \times 10^{-3}$ and $P_{\text{react}} \approx 5.5 \times 10^{-16}$.

3 Results and Discussion

The model predicts that reaction probability depends exponentially on both temperature and activation free energy. A modest temperature increase from 280 K to 360 K (Fig. 1) raises by nearly six orders of magnitude. This demonstrates the strong thermokinetic sensitivity of molecular self-organization to thermal gradients.

Figure 2 confirms that decreasing ΔG^\ddagger by only 20 kJ mol⁻¹ enhances the probability by approximately five orders of magnitude. Such behavior suggests that even slight catalytic or environmental reductions in barrier height could dramatically accelerate prebiotic synthesis.

The exponential dependence of reaction probability on temperature agrees with classical Boltzmann statistics [Atkins and de Paula, 2010] and with thermodynamic interpretations of molecular self-organization [Eigen, 1971]. Such exponential sensitivity supports the hypothesis that local thermal gradients could facilitate prebiotic synthesis, as previously proposed by Smith and Lee [2021].

4 Conclusion

The presented model unifies microstate probability, Gibbs free energy, and reaction kinetics within a single statistical framework. Such an approach may offer predictive insight into the environmental and energetic constraints of early prebiotic chemistry.

5 Validation and Future Work

Future studies will incorporate experimental reaction-rate data and molecular dynamics simulations to validate the probabilistic predictions presented here. In particular, comparing computed P_{react} values with measured rate constants in condensation and polymerization reactions will test whether microstate-based probability scaling correctly reproduces empirical kinetics.

6 Graphs and Data

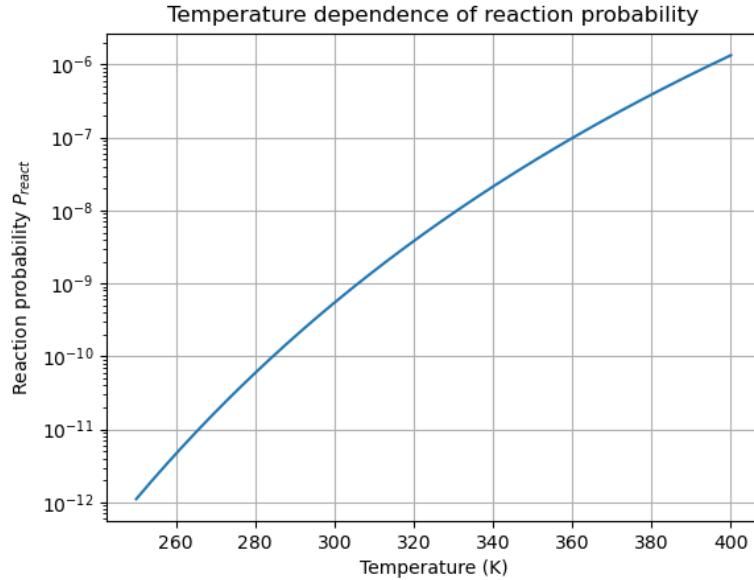


Figure 1: Temperature dependence of the reaction probability P_{react} calculated for $\Delta G^\ddagger = 75$ kJ mol⁻¹ and $k_{\text{max}} = 10^9$ M⁻¹ s⁻¹. The semilog plot illustrates the exponential increase in probability with temperature, consistent with the Boltzmann factor dependence $P_{\text{react}} \propto e^{-\Delta G^\ddagger/RT}$.

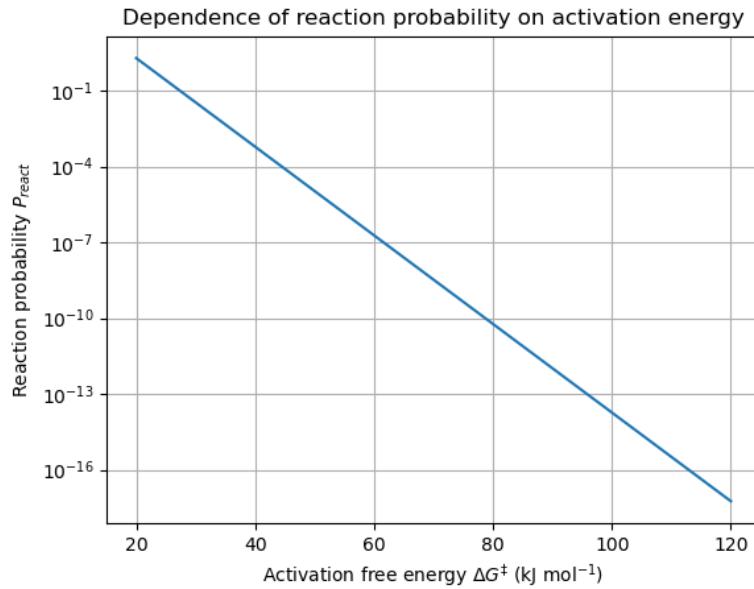


Figure 2: Dependence of the reaction probability on the activation free energy ΔG^{\ddagger} at $T = 298$ K. Higher energy barriers reduce P_{react} exponentially, highlighting the sensitivity of prebiotic kinetics to catalytic or environmental effects.

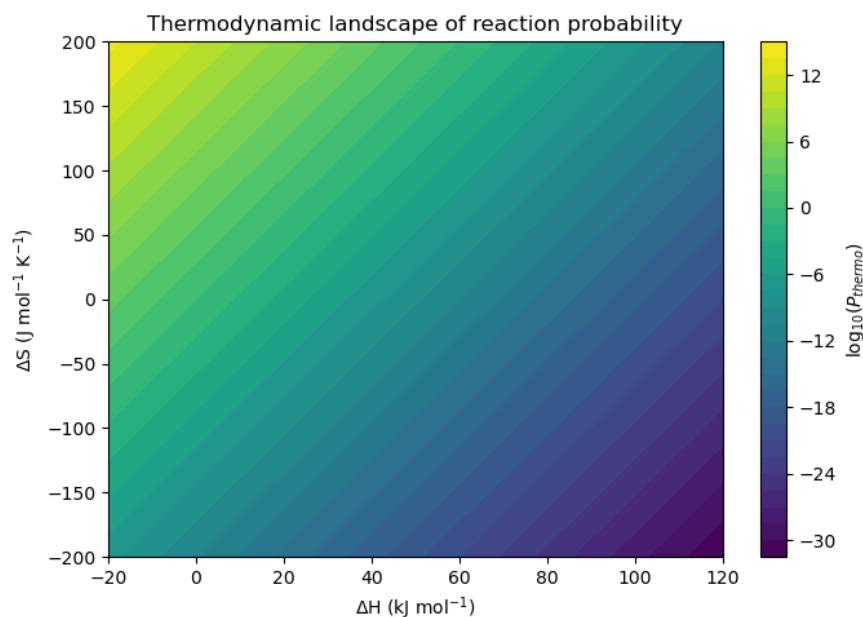


Figure 3: Contour plot showing the combined influence of enthalpy and entropy on the thermodynamic reaction probability $P_{\text{thermo}} = \exp[-(\Delta H - T\Delta S)/(RT)]$. Regions of high probability (yellow) correspond to energetically favorable and entropy-driven reactions, illustrating the interplay between enthalpic and entropic factors in prebiotic chemistry.

References

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