

## Electrons, kinetics, and entropy: unlocking the full potential of plasma-based gas conversion

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### 1. Introduction

Plasma-based gas conversion broadly falls into two main categories: (i) low-temperature (< 1000 K) transformation of gases into value-added chemicals, such as C<sub>2</sub> and C<sub>3</sub> from CH<sub>4</sub>, CH<sub>3</sub>OH from CO<sub>2</sub>, and NH<sub>3</sub> from N<sub>2</sub> and H<sub>2</sub>, for direct use in the chemical industry, and (ii) high-temperature (> 1000 K) decomposition of gases into smaller molecules or atoms, such as CO<sub>2</sub> into CO and O<sub>2</sub>, and CH<sub>4</sub> into C(s) and H<sub>2</sub>, which typically requires further processing (e.g. Fischer-Tropsch and methanol synthesis). The first category primarily involves plasma-catalysis, combining plasma reactors with catalysts at elevated gas temperatures (400–800 K). In contrast, the second category is mostly driven by non-equilibrium "warm" discharges, operating at 1000–5000 K and dominated by thermal reactions rather than electron-induced reactions. These observations raise two fundamental questions. (i) How does gas temperature affect reaction kinetics in plasma processes? (ii) If thermal effects appear dominant, does plasma still offer unique thermodynamic benefits, or is it simply an efficient heat source? Resolving these questions is essential for improving our understanding and optimizing gas conversion applications.

### 2. Results and Discussion

#### 2.1 Temperature-Dependent Kinetics

Temperature-dependent studies [1–3] reveal that reaction pathways and conversion in plasma-based gas processing are strongly influenced by the gas temperature (Fig. 1). In plasma-catalytic systems, for instance, elevated temperatures not only accelerate reaction rates but also influence reaction selectivity, shifting the balance among competing pathways.

While electron-induced reactions often dominate at low temperatures, thermal reactions play a more prominent role as the temperature increases. In some scenarios, thermal chemistry reinforces electron-driven pathways, while in others, it competes with them. Hence, developing temperature-dependent plasma-chemical reaction models is essential to accurately understand conversion rates and selectivities across different temperature regimes. These mechanistic insights help identify the optimal operating window for plasma-based gas conversion processes, maximizing the synergy between thermal and electron-driven effects for improved performance.

#### 2.2 Non-Equilibrium Thermodynamics

Recently, an effective (average) energy input ( $E_{in} = \sqrt{E_{pl}} \times \sqrt{E_{heat}}$ ) related to the entropy change under non-equilibrium conditions—at (constant) temperature—was proposed as a key parameter controlling plasma reactions

[4,5]. At high gas temperatures, certain plasma processes that seem governed by thermal chemistry, still deviate from classical expectations. This is manifested as enhanced conversions and energy efficiencies relative to thermal equilibrium benchmarks.

Such behavior suggests additional non-equilibrium contributions. The contribution of entropy (at a constant temperature), that is  $T_e \Delta S_{m,e}$  and  $T_{gas} \Delta S_{m,T}$ , as the fundamental parameter in plasma gas conversion thus becomes integral to characterize the system [4].

### 3. Conclusions

In summary, plasma-based gas conversion is governed by an intricate balance of temperature-sensitive kinetics and non-equilibrium thermodynamics. Even under conditions where thermal chemistry appears dominant, plasma can modulate reaction pathways in ways that remain inaccessible under strict thermal equilibrium. A more fundamental understanding could stimulate further technological enhancements in plasma-based gas conversion.

### References

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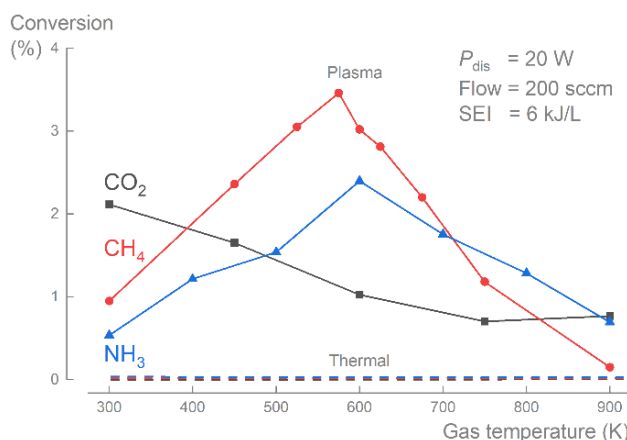


Figure 1. CO<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub> conversion for thermal (dashed lines) and plasma (solid lines) conditions in a temperature-controlled DBD. Data taken from [1–3].