# Reversible soot surface growth: Approximating PAH chemistry

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The aim of this work is to develop of a methodology to approximate PAHs growth rates that account for reversibility based on a systematic study of the reactions occurring within simple aromatic species.

## 1. Introduction

- Soot particles are formed during incomplete hydrocarbon combustion and have adverse effects on health and the environment.
- Polycyclic aromatic hydrocarbons (PAHs) are produced during combustion from gas phase species and are the main constituents of soot.
- PAHs in the gas phase have different growth pathways that can help us to understand how soot particles grow.
- Acetylene addition has been used to explain this phenomenon. However, it simplifies the process by assuming it is irreversible. The rate constants for this formulation were obtained from the benzene to naphthalene reactions [1].

$$r_{\substack{\text{soot}\\\text{growth}}} = 2\,\frac{\alpha\, k_4[C_2H_2]\,(k_1[H^\bullet]+k_2[HO^\bullet])\,[C_{sites}]}{k_{b1}[H_2]+k_{b2}[H_2O]+k_3[H^\bullet]+k_4[C_2H_2]}$$

$$C_s{-}H + H^\bullet \rightleftharpoons C_s^\bullet + H_2 \quad (1)$$
$$C_s{-}H + HO^\bullet \rightleftharpoons C_s^\bullet + H_2O \quad (2)$$
$$C_s^\bullet + H^\bullet \longrightarrow C_s{-}H \quad (3)$$
$$C_s^\bullet + C_2H_2 \longrightarrow C_s{-}C_2H + H \quad (4)$$

## 2. Methods

- Use of a combination of pre-equilibrium (PEQA) and quasi steady state approximations (QSSA) to obtain a better growth rate for PAHs.
- Define which reactions need to be included with a novel algorithm.
- Apply the methodology to the ABF mechanism [2] for ethylene/air combustion at different temperatures and equivalence ratios to determine quality of predictions.

**PAH growth rate algorithm**

1. Perform 0D simulations and flux analysis for the mechanism and conditions being studied.
2. Define species of interest: benzene and its intermediates to naphthalene.
3. Select important reactions with the formula:

$$\frac{1}{N}\sum_{i}^{N}\frac{\dot{q}_i}{\dot{Q}_i} \geq Tol$$

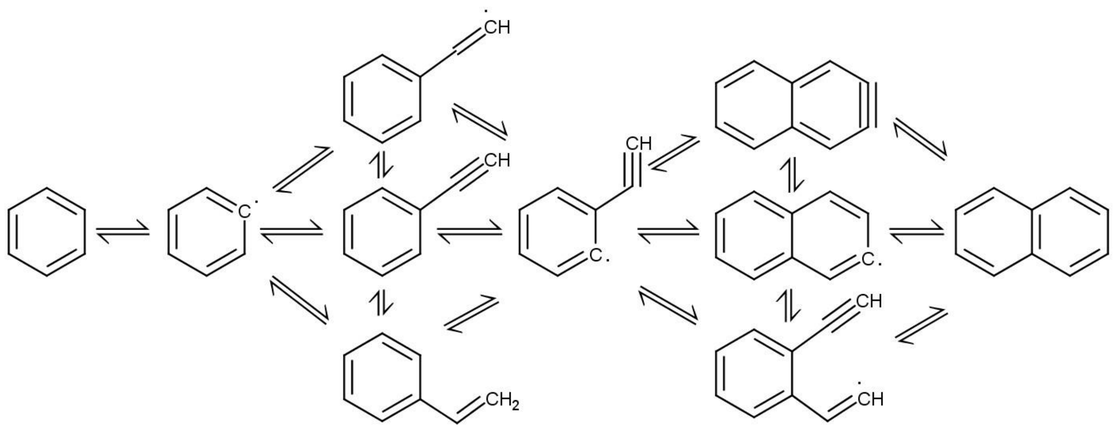
4. Solve the PAH chemistry for the defined species using the PEQA and QSSA:

$$\boldsymbol{Y} = \boldsymbol{M}^{-1}\,\boldsymbol{b}$$

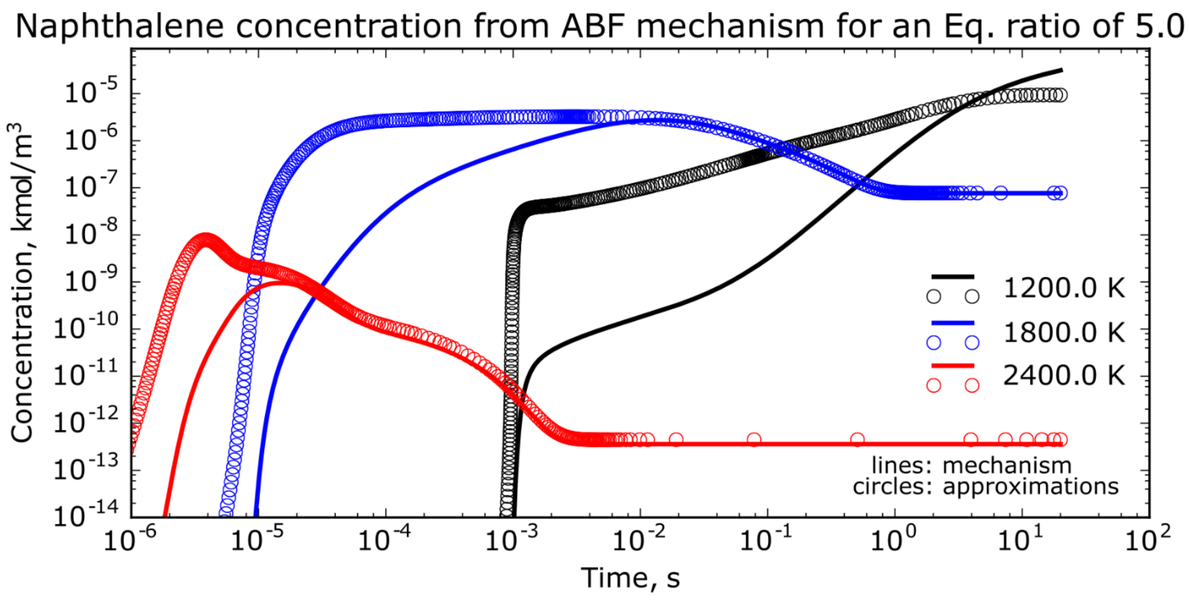
$\boldsymbol{M}$ → Stoichiometric matrix with selected reactions
$\boldsymbol{b}$ → Source terms vector for PAH chemistry

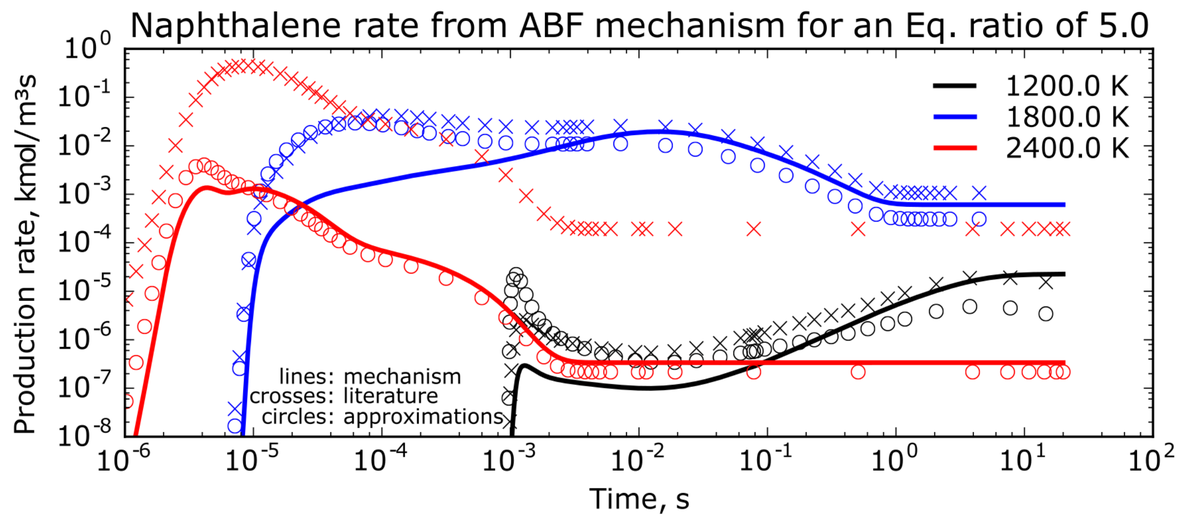
5. Validate the algorithm. Verify the sources of error inherent to the approximations through a timescale analysis [3].

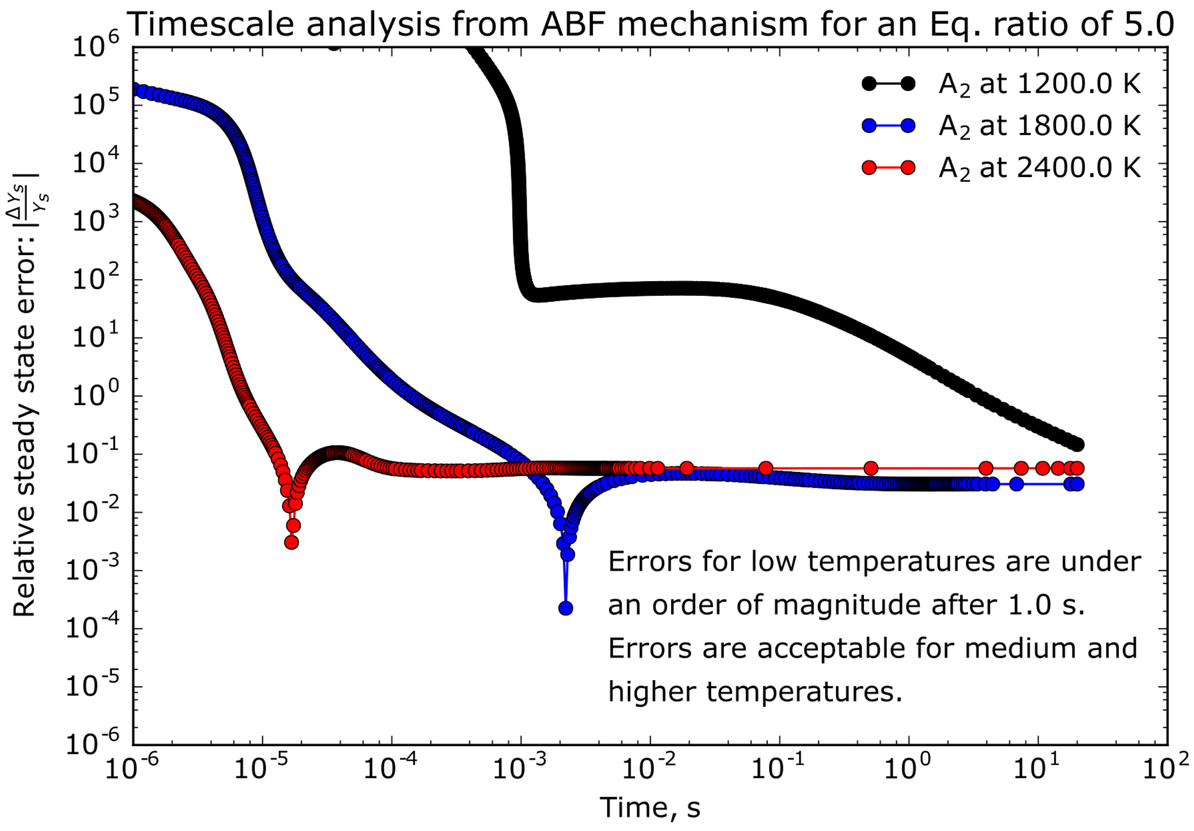
$$\tau_s = -\boldsymbol{J}_{ss}^{-1} \qquad |\Delta Y_s| = \left|\tau_s \frac{dY_s}{dt}\right|$$




## 3. Results




## 4. Conclusions

- The methodology developed provides improved approximations at high temperatures and keeps similar orders of magnitude for medium and low temperatures compared to previous rates used in literature.
- This methodology includes the reversible reactions between PAHs and the gas phase that have been previously omitted.

## 5. Future Work

- Use the growth rates obtained from this methodology in laminar flame applications.
- Replicate and compare the methodology for different mechanisms.
- Apply the methodology to study soot surface growth in Kinetic Monte Carlo (KMC) models.

## References

1. Roy, S. & Haworth, D. (2016). *Comb. Sci and Tech.*, *188(7)*, 1021-1053
2. Appel, J. *et al*. *Comb. and Flame*, *121*, 122-136
3. Turanyi, T. *et al.* (1993). *J. Phys. Chem.*, 97(1), 163-172