Chemical Kinetics and CVD of Graphene

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Chemical Kinetics - A Primer

- A chemical "reaction" between reactans and products indicates the mass balance in the reaction

$$A + B \longleftrightarrow C + D$$

  for instance, $O_2 + 2\,H_2 \longleftrightarrow 2\,H_2O$
- The *rate* at which the reaction happens depends on the *mechanism* of the reaction:
  - unimolecular reaction $A_2 \longrightarrow 2\,A$

$$\partial\left[A_2\right]/\partial t = k_{\rightarrow}\left[A_2\right]$$

  - bimolecular reaction $A + B \longrightarrow C + D$

$$\partial\left[A\right]/\partial t = k_{\rightarrow}\left[A\right]\left[B\right]$$

  - if the reaction is indicative of the mechanism $n\,A + m\,B \longrightarrow \ldots$

$$\partial\left[A\right]/\partial t = k_{\rightarrow}\left[A\right]^n\left[B\right]^m$$

- Chemical equilibrium can be found by balancing forward and backward rates

$$k_{\rightarrow}\left[A\right]\left[B\right] = k_{\leftarrow}\left[C\right]\left[D\right]$$

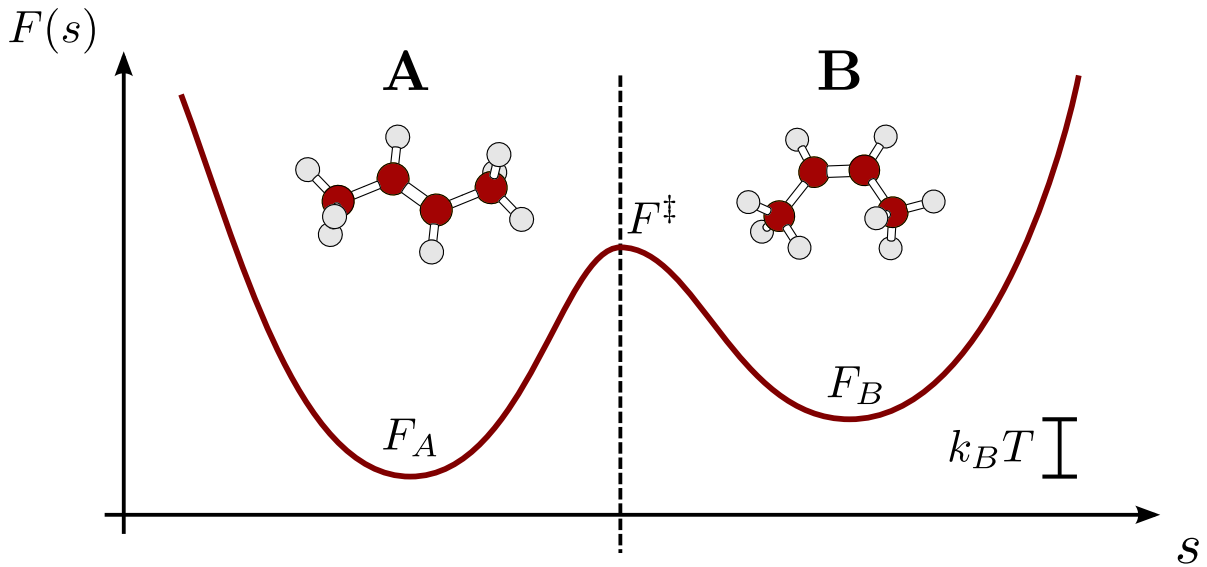
Transition-state theory

- Reactions often correspond to the system going through a high-(free)-energy *transition state* region
- Statistical mechanical treatment of the problem shows that rates can be approximated based on the barrier $F^{\ddagger} - F_A$

$$k_{\rightarrow} = \frac{1}{\tau} e^{-\left(F^{\ddagger} - F_A\right)/k_B T}, \qquad k_{\leftarrow} = \frac{1}{\tau} e^{-\left(F^{\ddagger} - F_B\right)/k_B T}$$

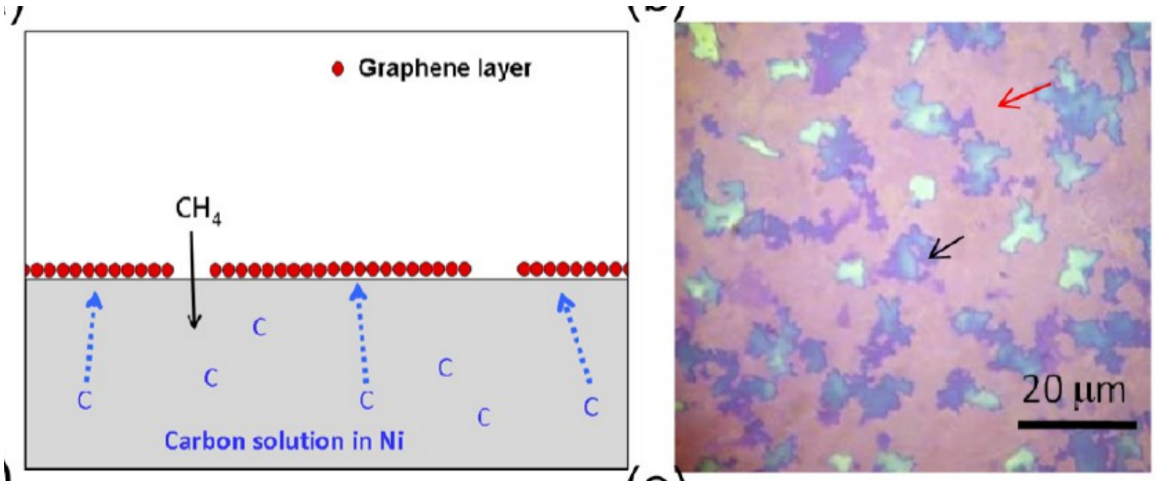
- This guarantees *detailed balance*: ratio of FW and BW rates corresponds to relative probability of A and B

$$k_{\rightarrow}/k_{\leftarrow} = e^{-(F_B - F_A)/k_B T}$$



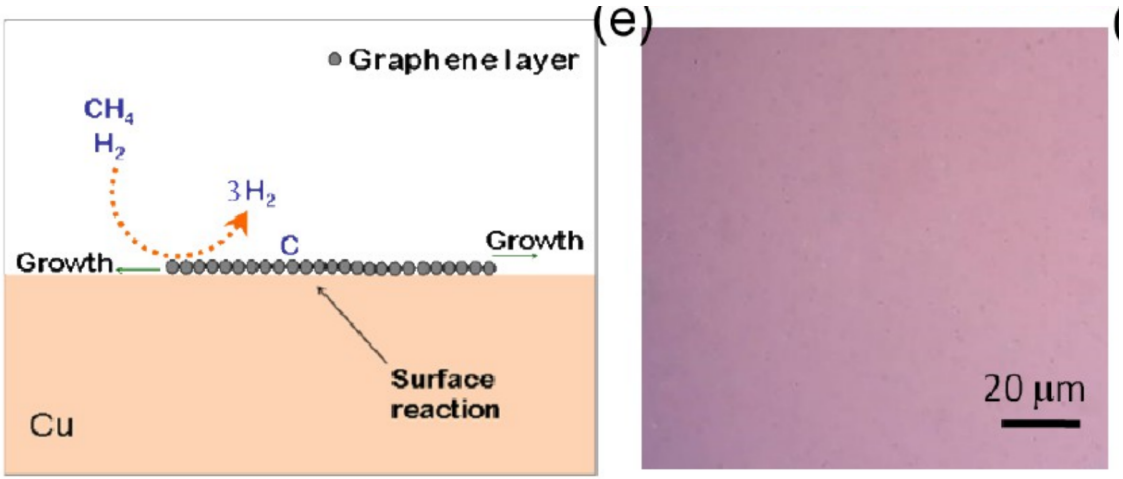
CVD of Graphene

- Graphene shows incredible fundamental and technological potential (1B€ flagship EU initiative)
- CVD offers an industrially-scalable synthesis protocol, using CH_4 as precursor
  - Using Ni catalyst - bulk diffusion of dissolved carbon ⇒ multi-layer graphene
  - Using Cu catalyst - surface-driven mechanism ⇒ single-layer graphene
- Fine-grained control of morphology is possible tuning substrate and process



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