Physical Chemistry for Energy Engineering

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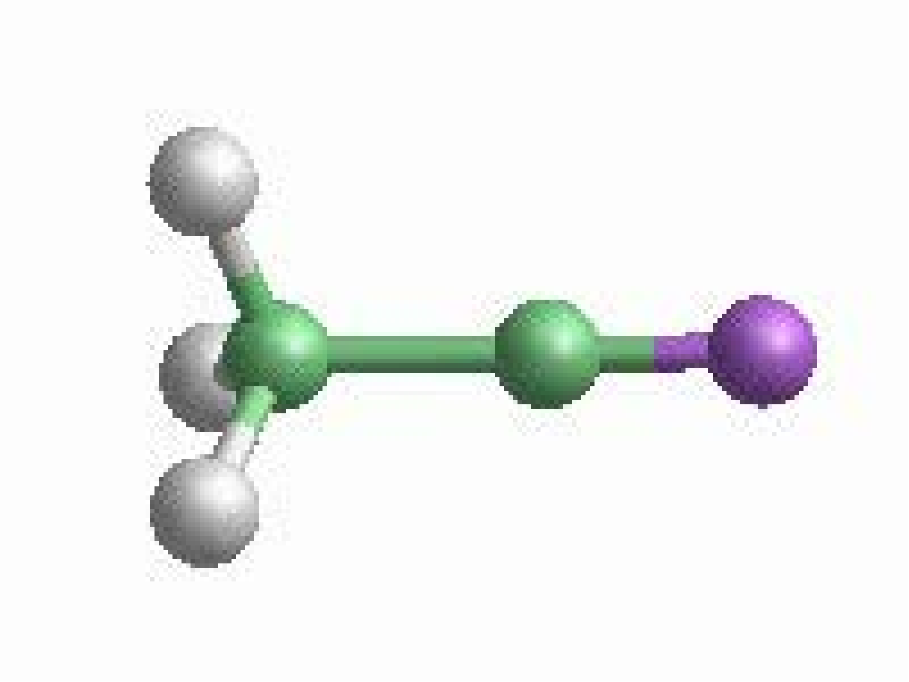
*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

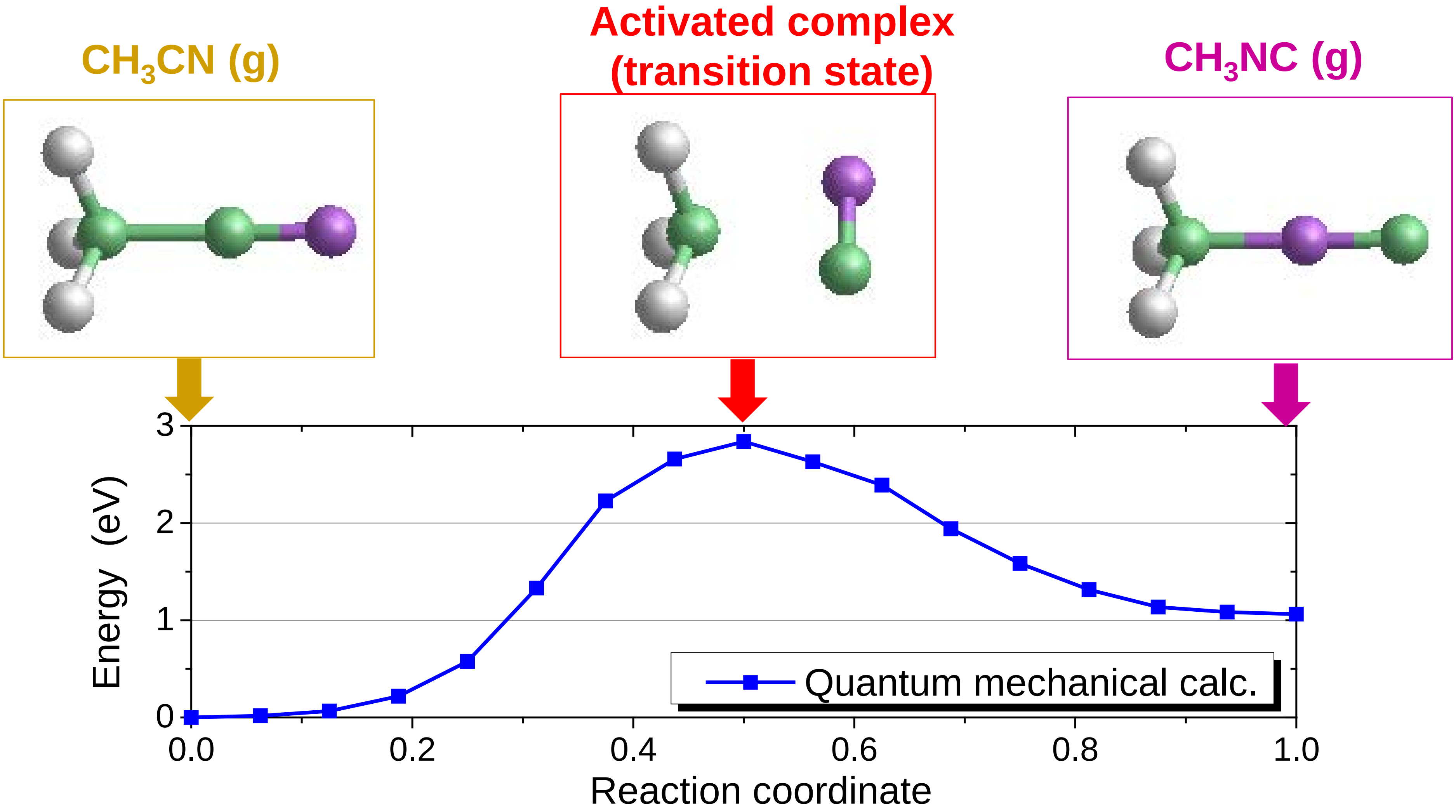
4.3. Chemical kinetics: reaction mechanisms

- $29.6: The Lindemann mechanism explains how uni-molecular reactions occur-

Quantum-mechanical calculation result on “$CH_3CN \rightarrow CH_3NC$” transformation



(Appendix) Study on the mechanism with Quantum mechanical calculation



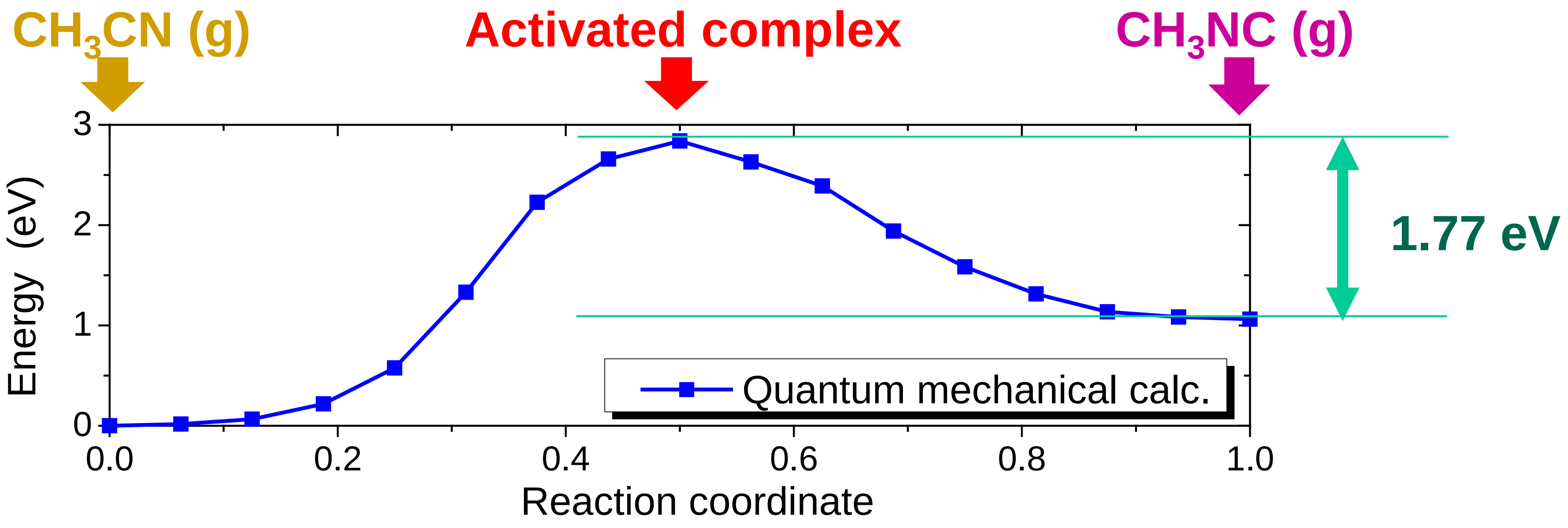
CH_3CN (g)

Activated complex (transition state)

CH_3NC (g)

(Quiz) How much is the activation energy for (1) transformation reaction from CH_3CN to CH_3NC, and (2) transformation reaction from CH_3NC to CH_3CN.

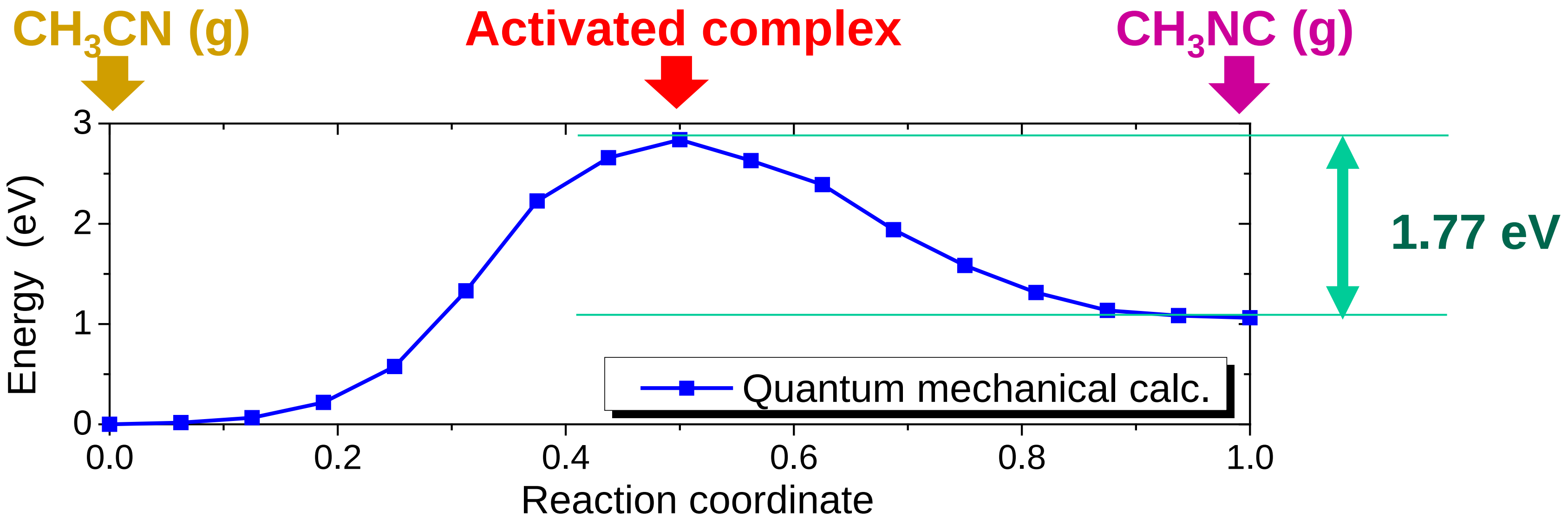
(Appendix) Study on the mechanism with Quantum mechanical calculation



The activation of transformation from CH_3NC to CH_3CN is 1.77 eV in calculation, while 1.35 eV in experiment as Arrhenius-type activation energy.

- ✓ Error in quantum mechanical calculation. As you know, the exact solution of Schrodinger equation is only achieved for some very simple cases. To calculate this kind of molecule, we use some approximations, which usually bring some error.
- ✓ We may miss an important path from CH_3NC to CH_3CN, which has a smaller activation energy.

(Appendix) Energy unit conversion



In physics, we usually use [eV] for energy unit, not [kJ/mol]

- ✓ Although we do not specify, [eV] usually means [eV/reaction], [eV/atom], [eV/molecule].
- ✓ In the previous slide, 1.77 eV of activation energy means "we need to give 1.77 eV to a CH_3NC molecule for its transformation to a CH_3CN molecule at least".

To convert [eV] to [kJ/mol], we first convert eV unit to kJ unit and then multiply it with 6.02E23 to make it per mol value.

1.77 [eV/atom] x (1.6E-19 [J/eV] x 6.02E23 [atoms/mol] / 1000)
= 170 [kJ/mol]

4.3. Chemical kinetics: reaction mechanisms

- some examples-

(#29-13) O_2NNH_2 decomposes in water according to the chemical equation

$O_2NNH_2(aq) \rightarrow N_2O(g) + H_2O(l)$ with k_{obs}

The experimentally determined rate law is: $\frac{d[N_2O]}{dt} = k_{obs}\frac{[O_2NNH_2]}{[H^+]}$

A proposed mechanisms for this reaction is:

$O_2NNH_2(aq) \mathrel{\substack{\Longrightarrow \\ \Longleftarrow}} O_2NNH^-(aq) + H^+(aq)$ *with* k_1 *for* $\Longrightarrow$ *&* k_{-1} *for* $\Longleftarrow$

$O_2NNH^-(aq) \Longrightarrow N_2O(g) + OH^-(aq)$ *with* k_2

$H^+(aq) + OH^-(aq) \Longrightarrow H_2O(l)$ *with* k_3

where the first step achieves an quasi-equilibrium immediately ("fast-equilibrium approximation"), the second step is slow, and the third step is fast. Show the relationship between k_{obs} *and the rate constants of the elementary reactions.*

The equilibrium constant for the first step is written as:

$$K_C = \left([O_2NNH^-]_{eq}[H^+]_{eq}\right)/[O_2NNH_2]_{eq} = k_1/k_{-1}$$

where we use $k_1[O_2NNH_2]_{eq} = k_{-1}[O_2NNH^-]_{eq}[H^+]_{eq}$ at equilibrium state.

The overall rate law is written from the equation of the second step

$$v = \frac{d[N_2O]}{dt} = k_2[O_2NNH^-]$$

4.3. Chemical kinetics: reaction mechanisms

- some examples-

(#29-13) $O_2NNH_2(aq) \rightarrow N_2O(g) + H_2O(l)$ with k_{obs}

The experimentally determined rate law is: $\frac{d[N_2O]}{dt} = k_{obs}\frac{[O_2NNH_2]}{[H^+]}$

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where the first step achieves an quasi-equilibrium immediately, the second step is slow, and the third step is fast. Show the relationship between k_{obs} *and the rate constants of the elementary reactions.*

$$K_C = \left([O_2NNH^-]_{eq}[H^+]_{eq}\right)/[O_2NNH_2]_{eq} = k_1/k_{-1}$$

$$v = \frac{d[N_2O]}{dt} = k_2[O_2NNH^-]$$

According to the fast-equilibrium approximation for the first step

$$([O_2NNH^-][H^+])/[O_2NNH_2] \sim \left([O_2NNH^-]_{eq}[H^+]_{eq}\right)/[O_2NNH_2]_{eq} = K_C = k_1/k_{-1}$$

Hence, $v = \frac{d[N_2O]}{dt} = k_2[O_2NNH^-] = \frac{k_2k_1}{k_{-1}}\frac{[O_2NNH_2]}{[H^+]}$.

In comparison with the experimentally-determined one, $k_{obs} = \frac{k_2k_1}{k_{-1}}$.

4.3. Chemical kinetics: reaction mechanisms

- some examples-

(#29-17) The rate law for the reaction described by

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$ with k_{obs}

is $d[N_2]/dt = k_{obs}[H_2][NO]^2$

Below is a proposed mechanism for this reaction

$H_2(g) + NO(g) + NO(g) \Rightarrow N_2O(g) + H_2O(g)$ with k_1

$H_2(g) + N_2O(g) \Rightarrow N_2(g) + H_2O(g)$ with k_2

Express k_{obs} using the rate constant for the individual steps of the mechanism.

The rate law is described based on the second step:

$$d[N_2]/dt = k_2[H_2][N_2O]$$

We assume the steady-state approximation can be used for N_2O, considering $k_2 \gg k_1$ because the second reaction is of bi-molecules while the first reaction is of tri-molecules.

$$d[N_2O]/dt = k_1[H_2][NO]^2 - k_2[H_2][N_2O] = 0$$

$$[N_2O] = (k_1/k_2)[NO]^2$$

Applying this result to the rate law of the overall reaction:

$$d[N_2]/dt = k_2[H_2] \times (k_1/k_2)[NO]^2 = k_1[H_2][NO]^2$$

Thus, $k_{obs} = k_1$

4.3. Chemical kinetics: reaction mechanisms

- $29.7: Some reaction mechanisms involve chain reactions -

Consider a reaction: $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

The experimentally determined rate law is:

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1+k'[HBr][Br_2]^{-1}}$$

where k and k' are rate constants.

✓ This rate law depends on both the reactant and product concentrations.

✓ Because the product appears in the denominator of the rate expression, its accumulation decreases the reaction rate.

✓ Detailed kinetic studies proposed the following elementary reactions in it:

(1) Initiation:	$Br_2(g) + M(g) \Rightarrow 2Br(g) + M(g)$	*with* k_1
(2) Propagation:	$Br(g) + H_2(g) \Rightarrow HBr(g) + H(g)$	*with* k_2
(3)	$H(g) + Br_2(g) \Rightarrow HBr(g) + Br(g)$	*with* k_3
(4) Inhibition:	$HBr(g) + H(g) \Rightarrow Br(g) + H_2(g)$	*with* k_{-2}
(5)	$HBr(g) + Br(g) \Rightarrow H(g) + Br_2(g)$	*with* k_{-3}
(6) Termination	$2Br(g) + M(g) \Rightarrow Br_2(g) + M(g)$	*with* k_{-1}

✓ Here M is a molecule that collides with the $Br_2(g)$ molecule, thereby imparting the energy necessary to break the chemical bond.

✓ One of the product of reaction 2 is a reactant in reaction 3, so called chain reactions. Reaction 4-

4.3. Chemical kinetics: reaction mechanisms

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(1) Initiation:	$Br_2(g) + M(g) \Rightarrow 2Br(g) + M(g)$	*with* k_1
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(3)	$H(g) + Br_2(g) \Rightarrow HBr(g) + Br(g)$	*with* k_3
(4) Inhibition:	$HBr(g) + H(g) \Rightarrow Br(g) + H_2(g)$	*with* k_{-2}
(5)	$HBr(g) + Br(g) \Rightarrow H(g) + Br_2(g)$	*with* k_{-3}
(6) Termination	$2Br(g) + M(g) \Rightarrow Br_2(g) + M(g)$	*with* k_{-1}

- ✓ The reaction (5) is endothermic by nearly 170 kJ mol^{-1}, while reaction(4) is exothermic by nearly 70 kJ mol^{-1}. Hence, it is reasonable to consider $k_{-3} \sim 0$.
- ✓ Because these 6 reactions are elementary reactions, we can write the rate laws ignoring the contribution of equation (5).

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] - k_{-2}[HBr][H] + k_3[H][Br_2]$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_{-2}[HBr][H] - k_3[H][Br_2]$$

$$\frac{d[Br]}{dt} = 2k_1[Br_2][M] - 2k_{-1}[Br]^2[M] - k_2[Br][H_2] + k_{-2}[HBr][H] + k_3[H][Br_2]$$

4.3. Chemical kinetics: reaction mechanisms

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$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1+k'[HBr][Br_2]^{-1}}$$

where k and k' are rate constants.

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] - k_{-2}[HBr][H] + k_3[H][Br_2]$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_{-2}[HBr][H] - k_3[H][Br_2]$$

$$\frac{d[Br]}{dt} = 2k_1[Br_2][M] - 2k_{-1}[Br]^2[M] - k_2[Br][H_2] + k_{-2}[HBr][H] + k_3[H][Br_2]$$

- ✓ Applying the steady-state approximation to [H] and [Br] gives us

$$k_2[Br][H_2] - k_{-2}[HBr][H] - k_3[H][Br_2] = 0$$

$$2k_1[Br_2][M] - 2k_{-1}[Br]^2[M] - k_2[Br][H_2] + k_{-2}[HBr][H] + k_3[H][Br_2] = 0$$

- ✓ Summing up these equations brings

$$2k_1[Br_2][M] - 2k_{-1}[Br]^2[M] = 0$$

- ✓ Then, solving this expression for [Br] gives us

$$[Br] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Br_2]^{1/2} = \left(K_{c,1}\right)^{1/2}[Br_2]^{1/2}$$

$$[H] = \frac{k_2 {K_{c,1}}^{1/2}[H_2][Br_2]^{1/2}}{k_{-2}[HBr]+k_3[Br_2]}$$

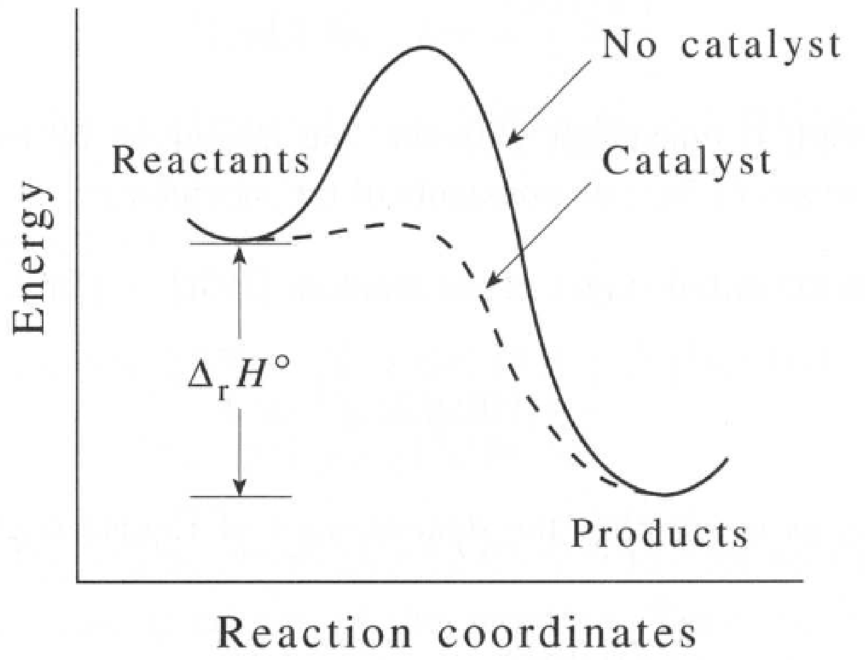
$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k_2 {K_{c,1}}^{1/2}[H_2][Br_2]^{1/2}}{1+(k_{-2}/k_3)[HBr][Br_2]^{-1}}$$

Applying "$k = k_2 {K_{c,1}}^{1/2}$" and "$k' = (k_{-2}/k_3)$" makes this equation identical to the experimental equation.

4.3. Chemical kinetics: reaction mechanisms

- $29.8: Some reaction mechanisms involve chain reactions -

- ✓ We can accelerate the rate of a reaction by changing temperature. But, it may bring un-desirable reactions: e.g. phase transition, decomposition, etc.
- ✓ Another way to modify the reaction rate is using a *catalyst*.
- ✓ A catalyst is a substance that participates in the chemical reaction but is not consumed in the process. A catalyst provides a new reaction mechanism of a smaller reaction barrier (activation energy).



- ➢ Note as the catalyst is not consumed, the exothermicity or endothermicity of the chemical reaction is not affected.
- ➢ As reaction rate depends exponentially on the activation barrier, a small change in the barrier results in a substantial change in the reaction rate.

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4.3. Chemical kinetics: reaction mechanisms

- $29.8: Some reaction mechanisms involve chain reactions -

Consider the reaction “A → products”.

$A \Rightarrow products$ *with* k

Addition of a catalyst creates new reaction pathway:

$A + catalyst \Rightarrow products + catalyst$ *with* k_{cat}

✓ If each of these competing reactions is an elementary process, the rate law for the overall reaction is given by the sum of the two terms:

$$-\frac{d[A]}{dt} = k[A] - k_{cat}[A][catalyst]$$

✓ In most cases, catalyst enhance reaction rates by many orders of magnitude, and therefore only the rate law for the catalyzed reaction need be considered in analyzing experimental data.

4.3. Chemical kinetics: reaction mechanisms

- $29.8: Some reaction mechanisms involve chain reactions -

- ✓ If the catalyst is in the same phase as the reactants and products, the reaction is called homogeneous catalysis. If different phase from the reactants and products, it is heterogeneous catalysis.

(Example of homogeneous catalysis) $O_3(g) + O(g) \Rightarrow 2O_2(g)$
If chlorine atoms exist, then it act as catalyst.

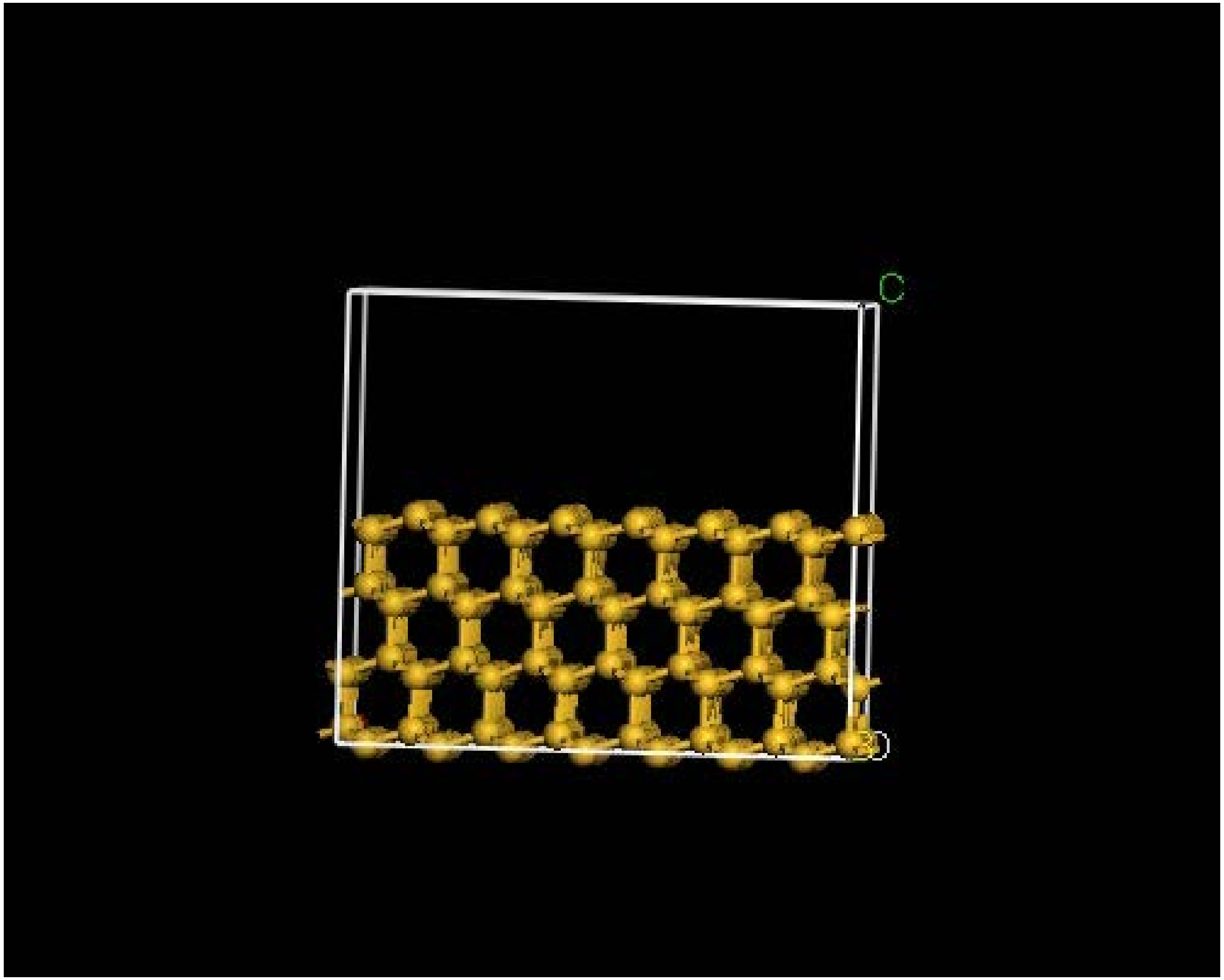
$$O_3(g) + Cl(g) \Rightarrow ClO(g) + O_2(g)$$
$$ClO(g) + O(g) \Rightarrow O_2(g) + Cl(g)$$

- ✓ The net result of this two-step cycle is the destruction of an ozone molecule without consuming the chlorine atom. Therefore, the chlorine atom is a catalyst for the ozone destruction reaction.

(Example of heterogeneous catalysis) $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$
If an iron surface exists as a catalyst, this reaction is largely accelerated.

- ✓ $\Delta_r G° = -32.4\ \mathrm{kJ}\ mol^{-1}$ at 300 K. However because the activation energy is roughly the decomposition energy of N_2 molecule (~940 kJ mol^{-1}), this ammonia synthesis reaction hardly occurs.
- ✓ However, if an iron surface exists, the barrier is lowered to ~80 kJ mol^{-1}.

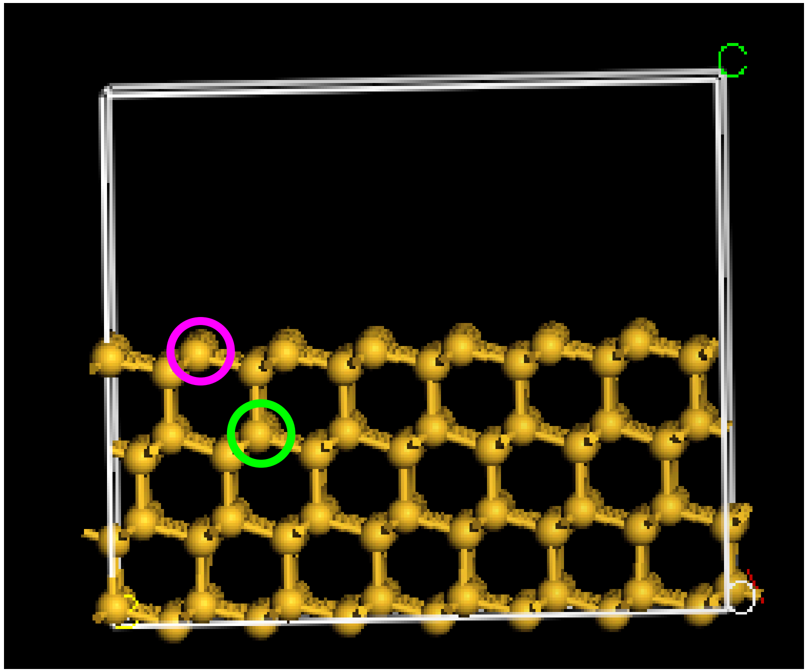
(Quiz) Why a surface often acts as a catalyst?



(Quiz) Why a surface often acts as a catalyst?

○ Atom on the surface

○ Atom in the bulk
(=inside the crystal)

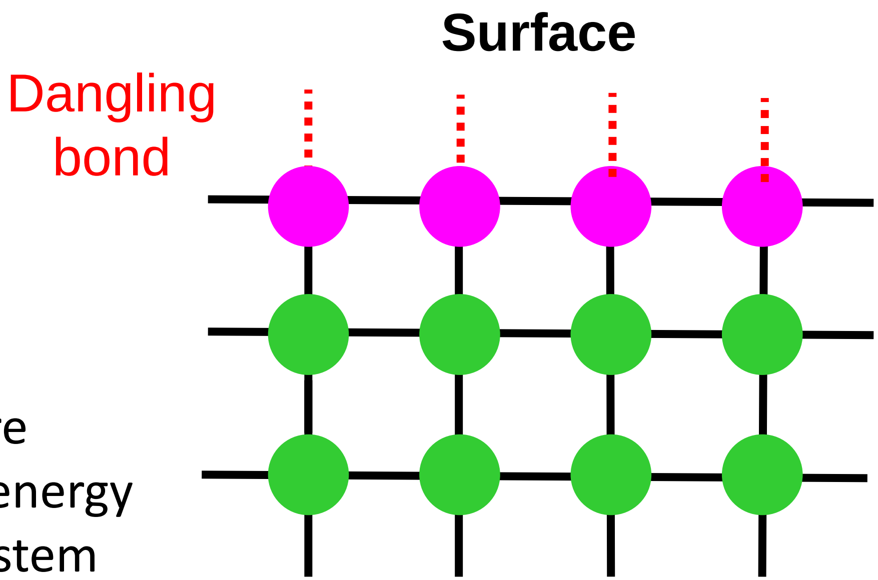


(Quiz) What are the difference between the surface atom and the bulk atom regarding the chemical bond?

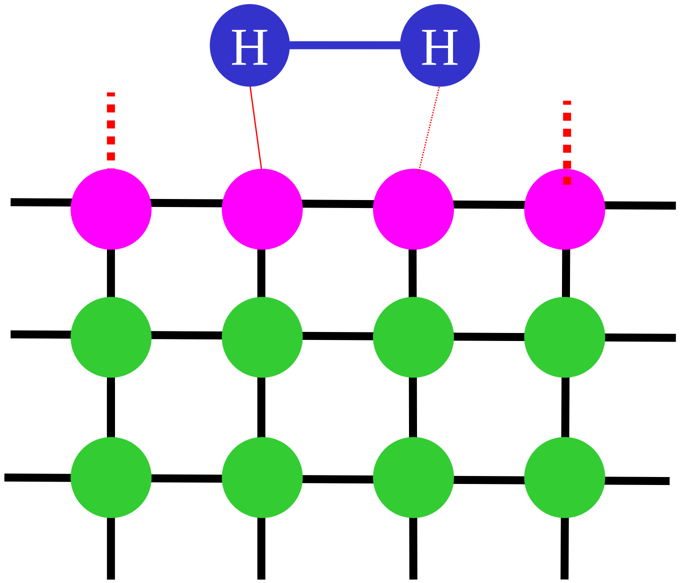
(Quiz) Why a surface often acts as a catalyst?

🟣 Atom on the surface

🟢 Atom in the bulk
(=inside the crystal)



- ✓ On the surface, interatomic bonds are abruptly terminated. Then, internal energy (U) is increased, which means the system becomes unstable, due to the existence of of surface.
- ✓ Such terminated bond is called “dangling bond”.
- ✓ If H_2 molecule is dissociated on the surface, the transition state can react with the dangling bond, which may make the transition state stable. In this case, the surface is regarded to act as a catalyst.



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