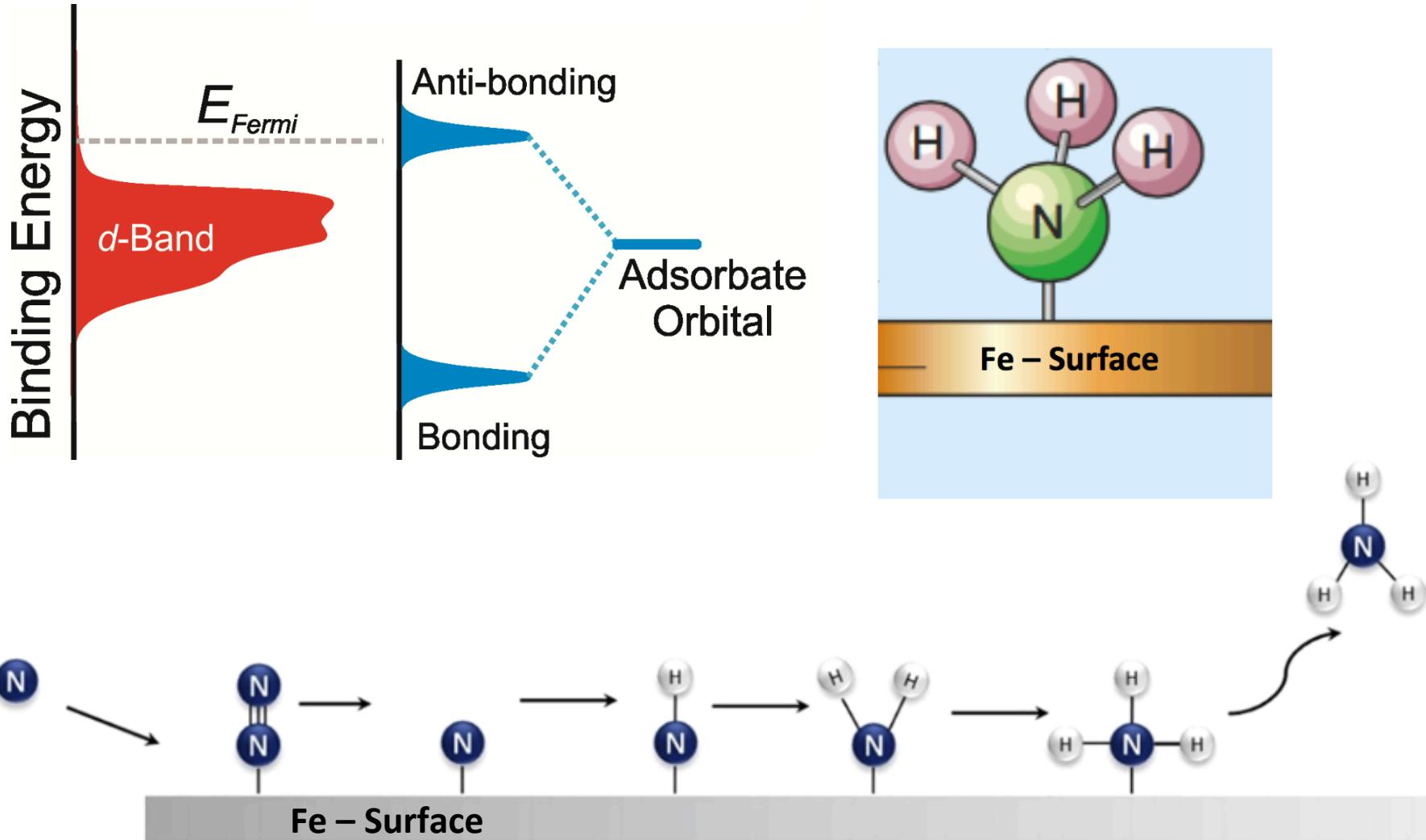


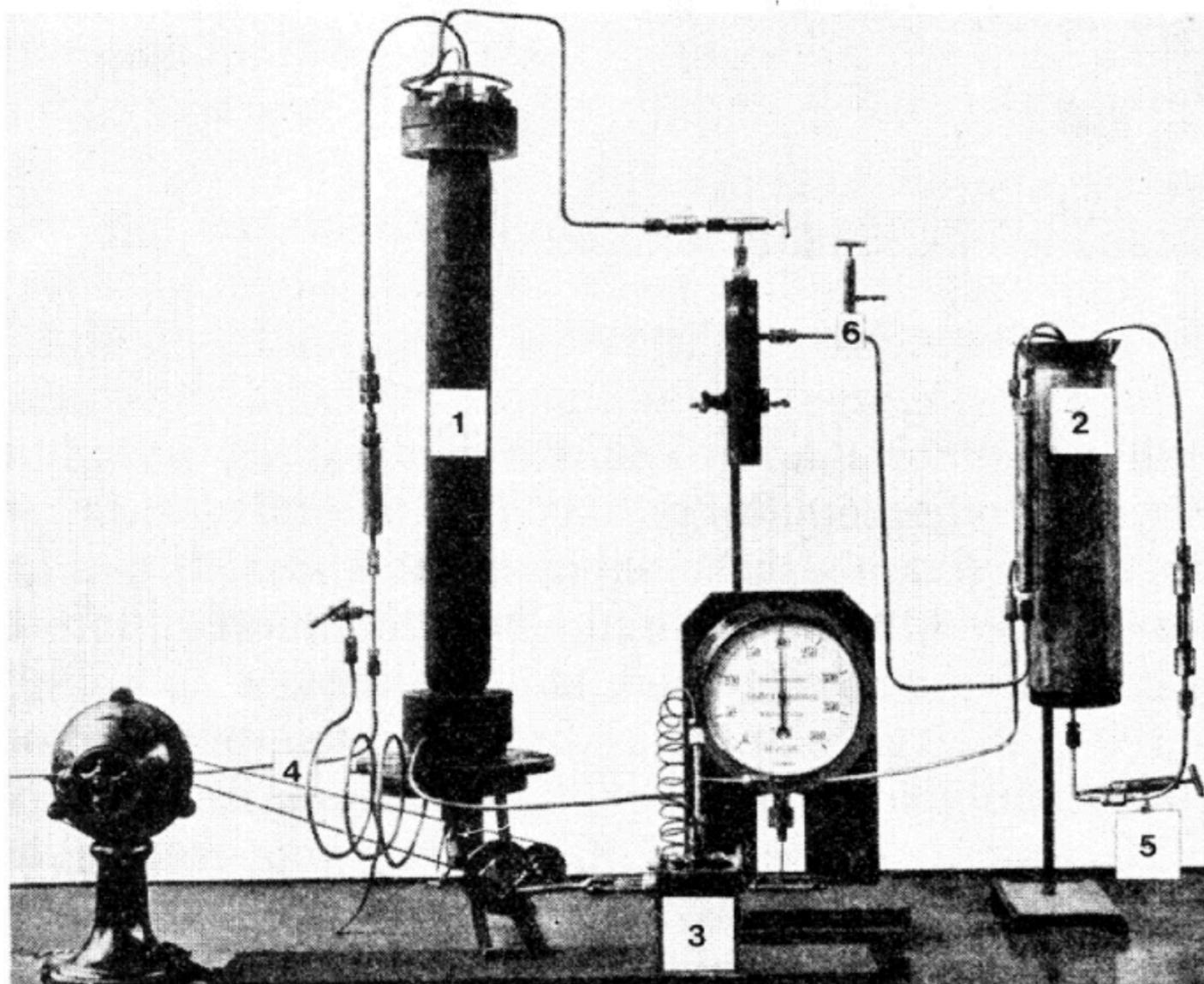
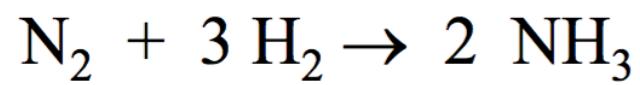
Chemical Processes.....





N₂ forms about 78% of Earth's atmosphere!

Nitrogen fixation means transformation of the abundant N₂ molecule (which constitutes about 80% of our air) from its state of very strong bond between the two N atoms into a more reactive form according to the reaction N₂ + 3H₂ → 2NH₃. This reaction of ammonia formation could be realized in 1909 by F. Haber (Nobel Prize 1919) in the laboratory by the use of an osmium catalyst in a high pressure flow apparatus [6]. C. Bosch (Nobel Prize 1931) from the BASF company started immediately to transform this process into technical scale, and the first industrial plant started operation in 1913, only a few years later. Fig. 3 shows the growth of the world population together with the ammonia production over the last century [7], and it is quite obvious that our present life would be quite different without the development of the Haber-Bosch process.



Haber & LeRossignol, 1909



Nitrogen is the most abundant element in the earth's atmosphere, and its conversion to ammonia is one of the highest volume industrial reactions. NH₃ is primarily used in fertilizers and also acts as a precursor to several other important chemicals such as nitric acid. NH₃ is also being considered as a carbon-free future fuel alternative.¹ Industrially, NH₃ is produced through the Haber Bosch (HB) process in which gaseous nitrogen and hydrogen react over an iron/ruthenium-based catalyst. The HB process is one of the most energy intensive chemical processes, consuming approximately 1%-1.5% of world energy.² By contrast, natural nitrogen fixation by diazotrophs, principally an electrochemical NH₃ synthesis reaction, is much more energy efficient.³ In a future with plentiful renewable electricity, an artificial electrochemical system to produce ammonia from nitrogen could be highly beneficial.

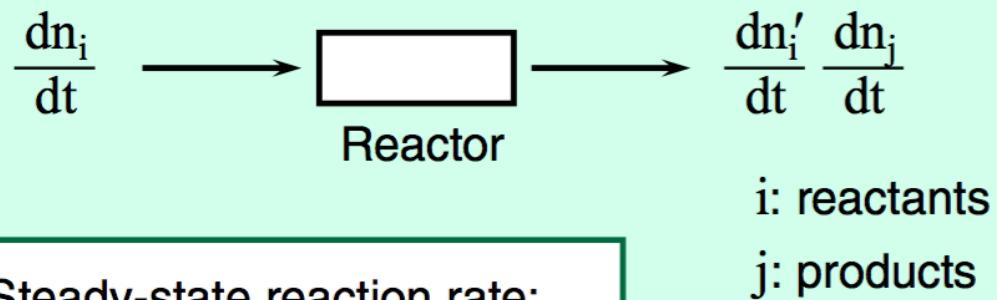
Possible heterogeneous catalysts for electrochemical nitrogen reduction (NRR) are currently marred by (1) the poor

However, large scale technical production would not have been possible without the availability of large quantities of a cheap catalyst. (The whole world supply of the precious metal osmium was only 80 kg in those days.) This task could be solved successfully by A. Mittasch [8] who in thousands of tests found that a material derived from a Swedish iron ore exhibited satisfactory activity. This type of doubly-promoted iron catalyst is in fact still in use today in almost all industrial plants.

Remarkably, despite the enormous technical significance of the Haber-Bosch reaction and despite of numerous laboratory studies its actual mechanism remained unclear over many years. P. H. Emmett, one of the pioneers of catalysis research, was honoured in 1974 by a symposium where he con-

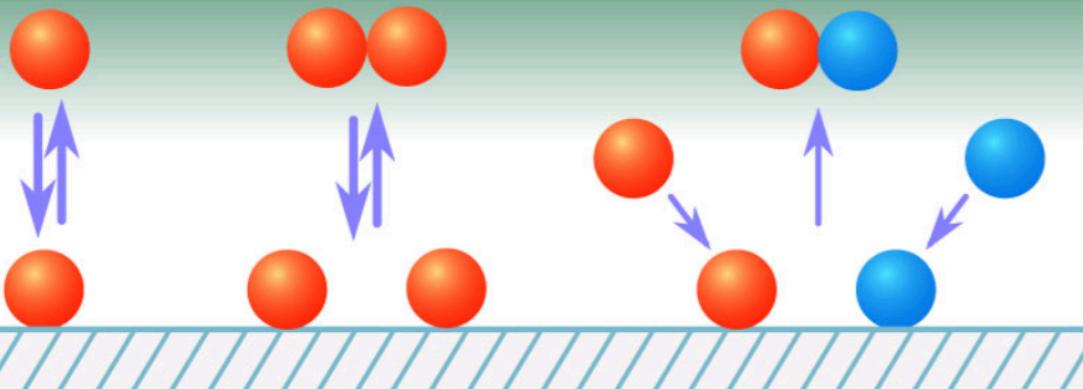
Remarkably, despite the enormous technical significance of the Haber-Bosch reaction and despite of numerous laboratory studies its actual mechanism remained unclear over many years. P. H. Emmett, one of the pioneers of catalysis research, was honoured in 1974 by a symposium where he concluded at the end [9]: "The experimental work of the past 50 years leads to the conclusion that the rate-limiting step in ammonia synthesis over iron catalysts is the chemisorption of nitrogen. The question as to whether the nitrogen species involved is molecular or atomic is still not conclusively resolved ...".

Heterogeneous catalysis



Steady-state reaction rate:

$$\frac{dn_j}{dt} = r = f(p_i, p_j, T, \text{catalyst})$$



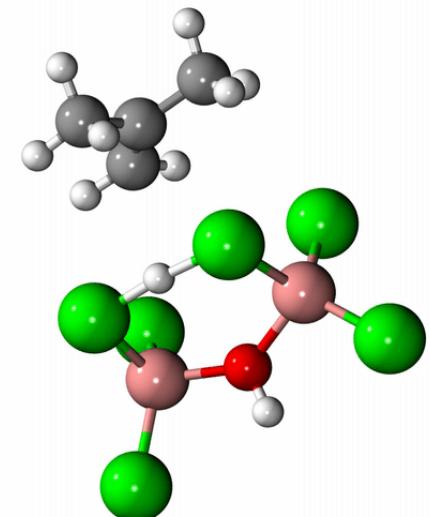
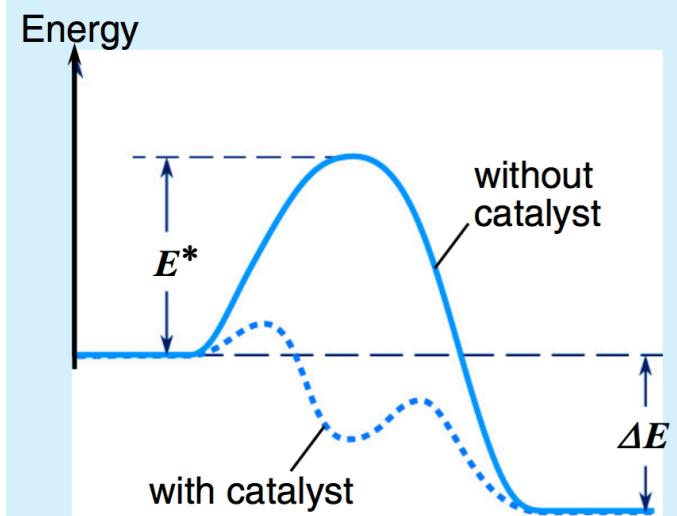
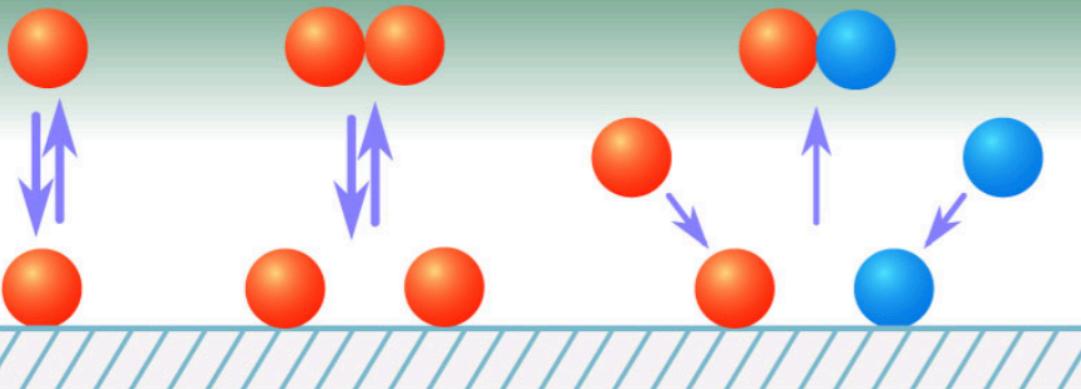
Heterogeneous catalysis

$$\frac{dn_i}{dt} \longrightarrow \boxed{\text{Reactor}} \longrightarrow \frac{dn'_i}{dt} \frac{dn_j}{dt}$$

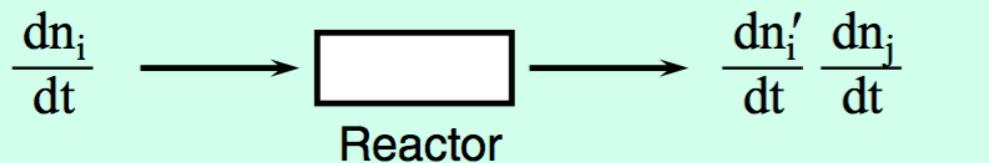
i: reactants
j: products

Steady-state reaction rate:

$$\frac{dn_j}{dt} = r = f(p_i, p_j, T, \text{catalyst})$$



Heterogeneous catalysis



i: reactants
j: products

Steady-state reaction rate:

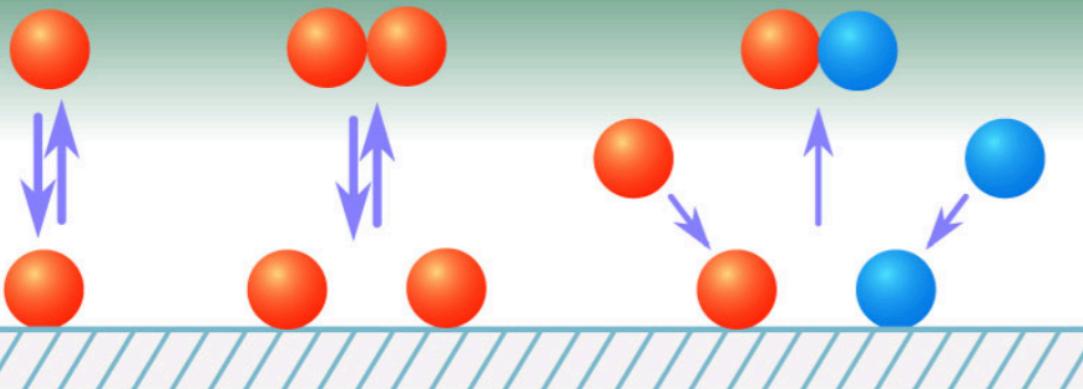
$$\frac{dn_j}{dt} = r = f(p_i, p_j, T, \text{catalyst})$$

Not all molecular encounters will be successful, but only a fraction $\exp(-E^*/kT)$.

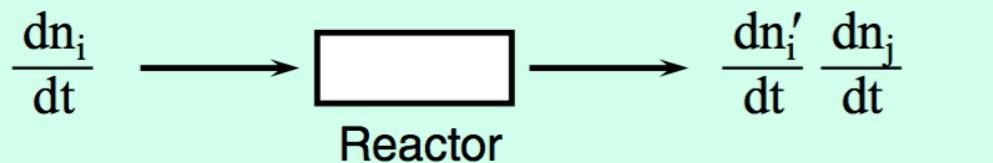


$$r = -\frac{d[A]}{dt} = k[A][B]$$

$$k = k_0 e^{-E^*/RT}$$



Heterogeneous catalysis



i: reactants
j: products

Steady-state reaction rate:

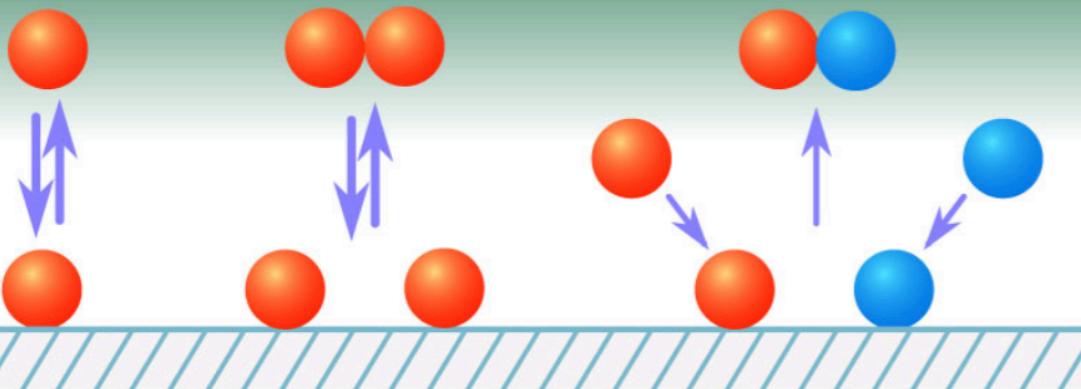
$$\frac{dn_j}{dt} = r = f(p_i, p_j, T, \text{catalyst})$$

Not all molecular encounters will be successful, but only a fraction $\exp(-E^*/kT)$.

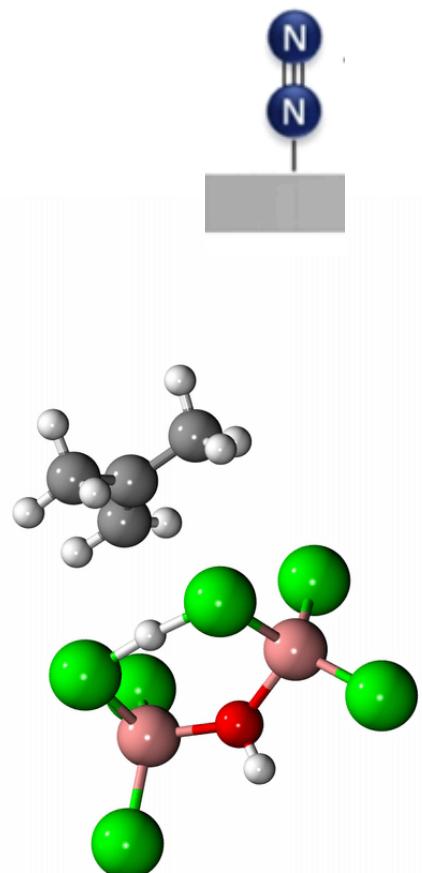
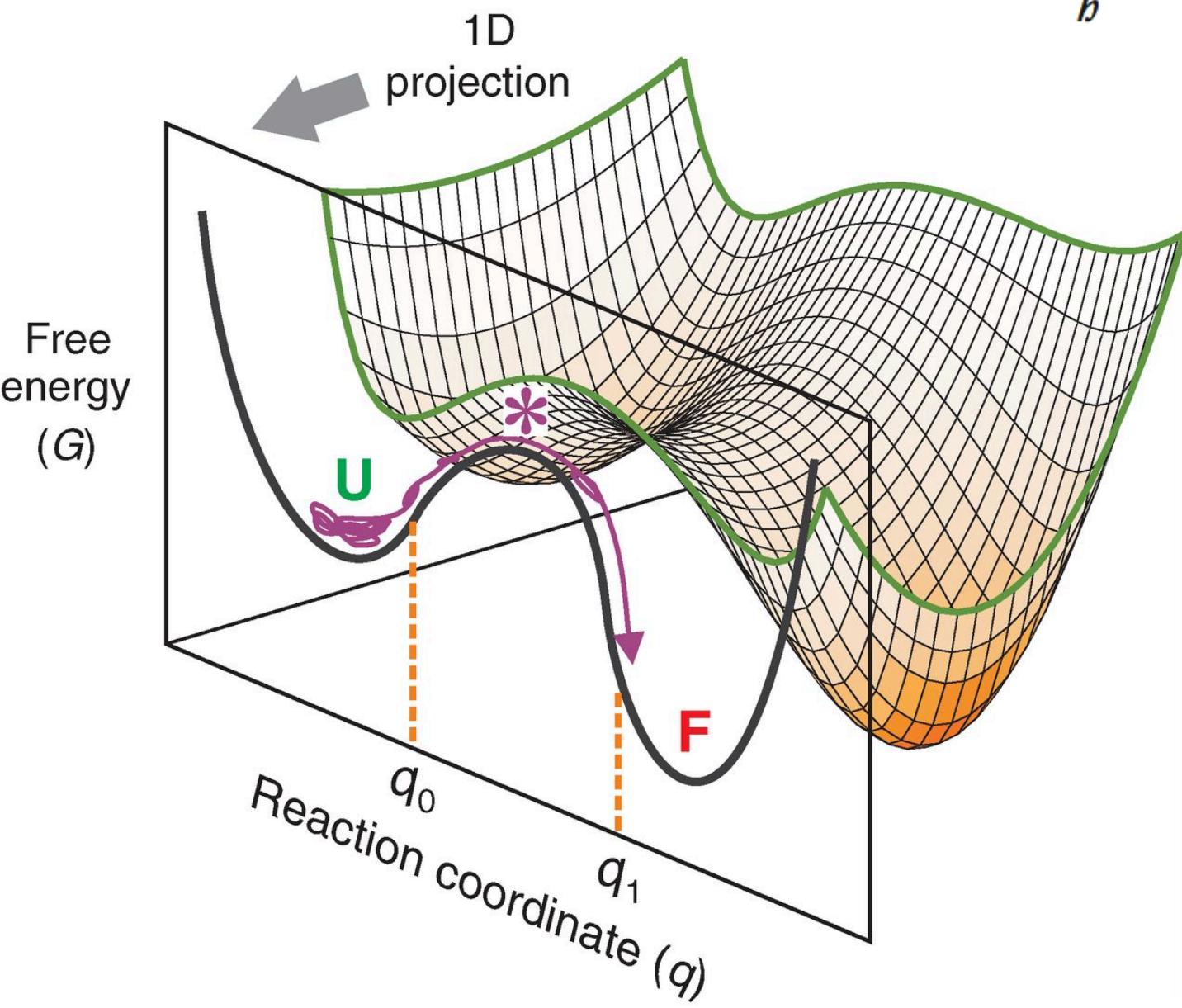


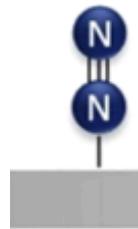
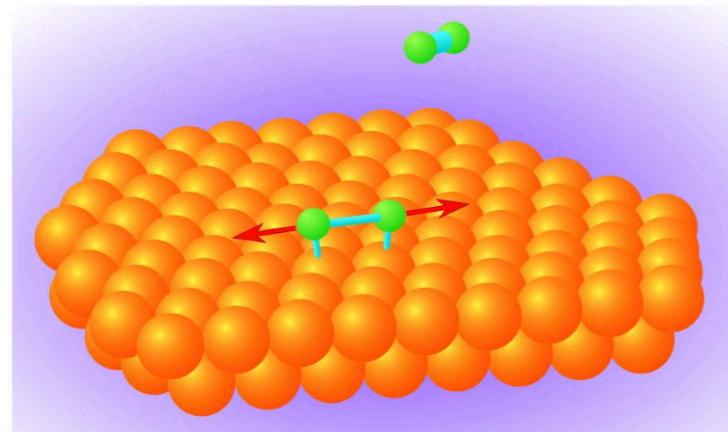
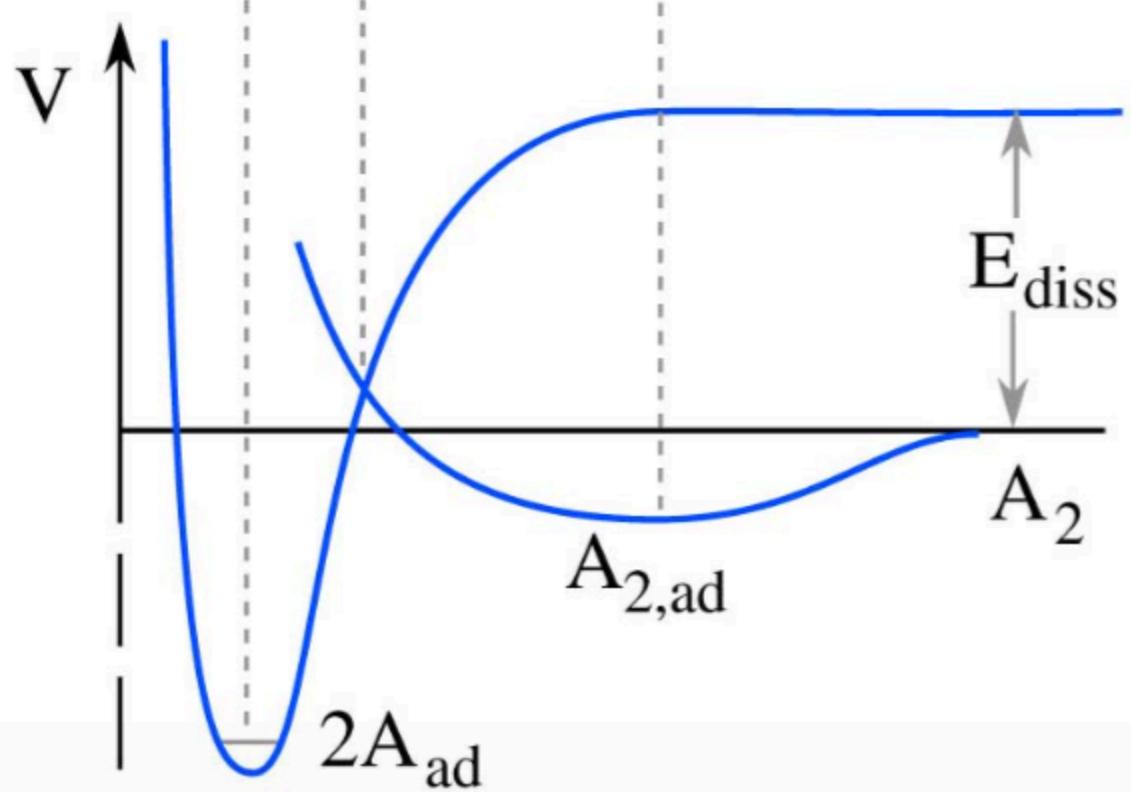
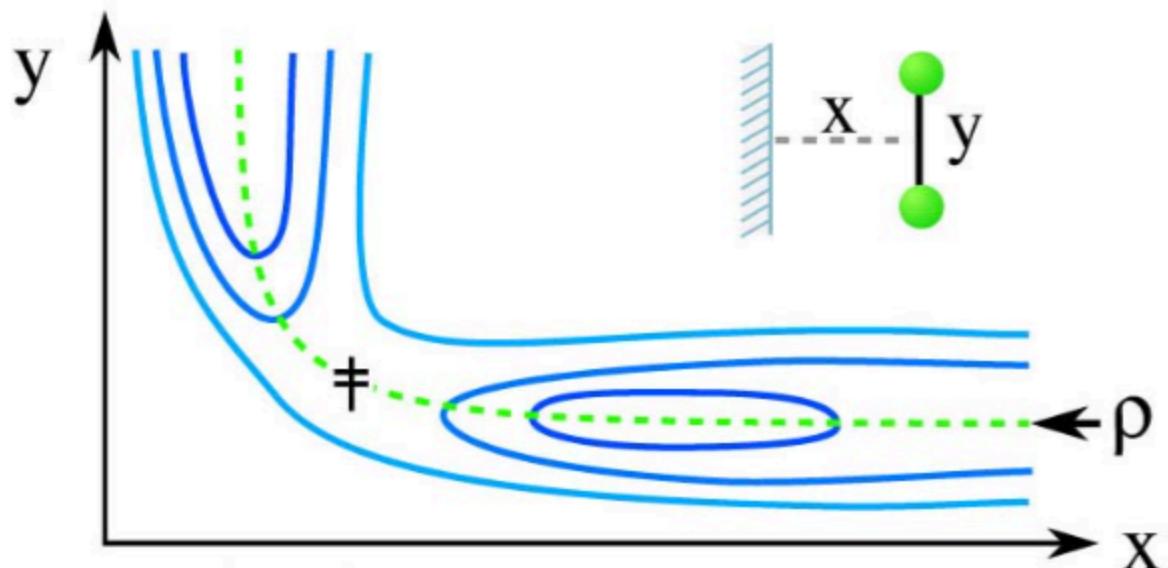
$$r = -\frac{d[A]}{dt} = k[A][B]$$

$$k = k_0 e^{-E^*/RT}$$

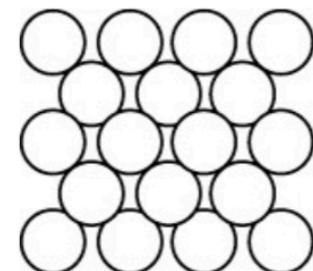
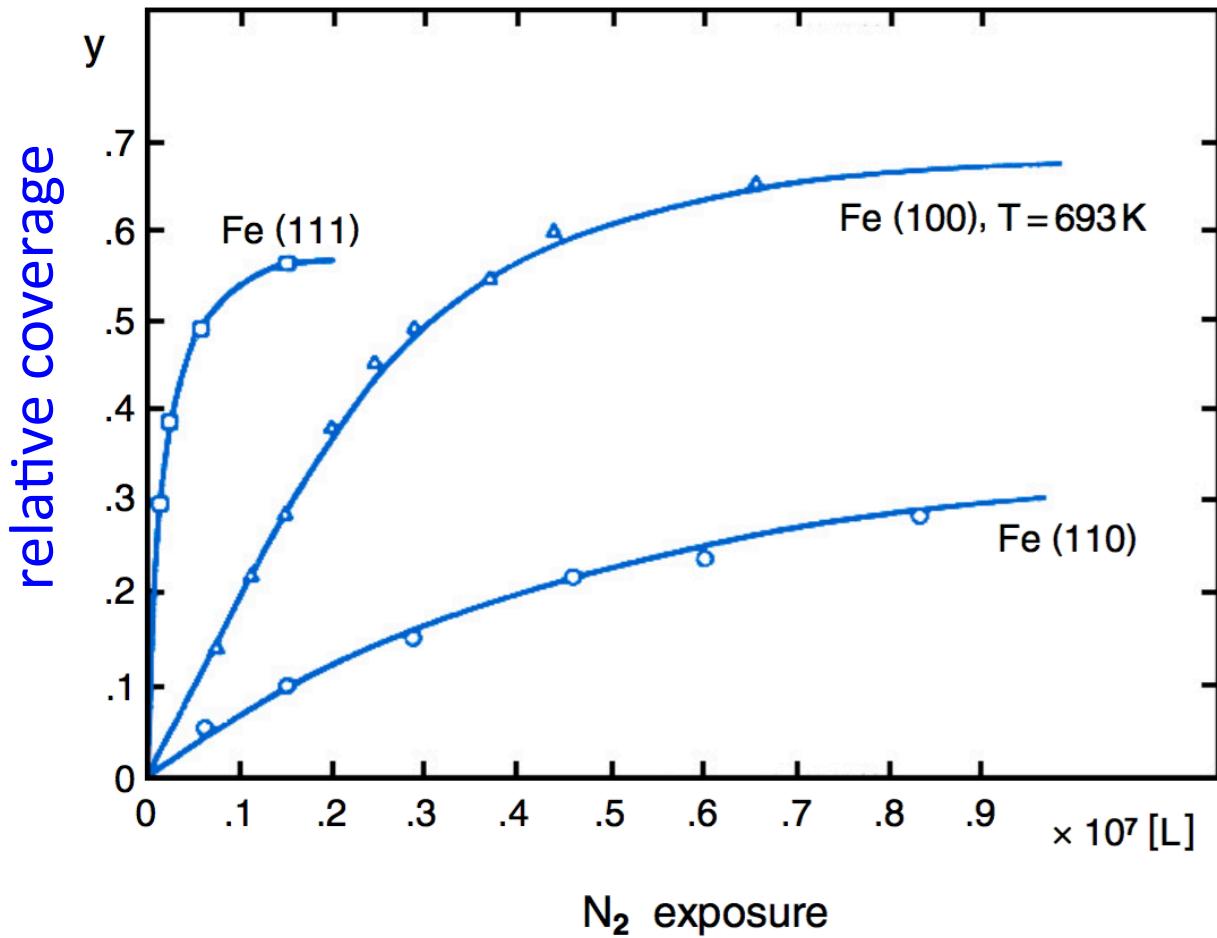


$$k_{\text{TST}} = \frac{k_{\text{B}} T}{b} (c^{\circ})^{\Delta v^\dagger} \exp\left(-\frac{\Delta G^{\circ\dagger}}{RT}\right)$$

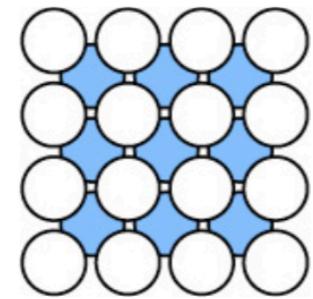




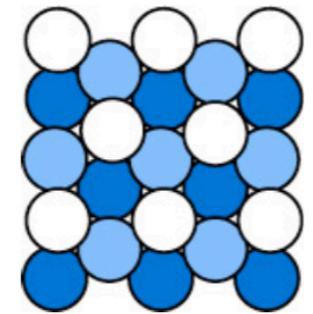
Dissociative nitrogen adsorption on Fe single crystal surfaces



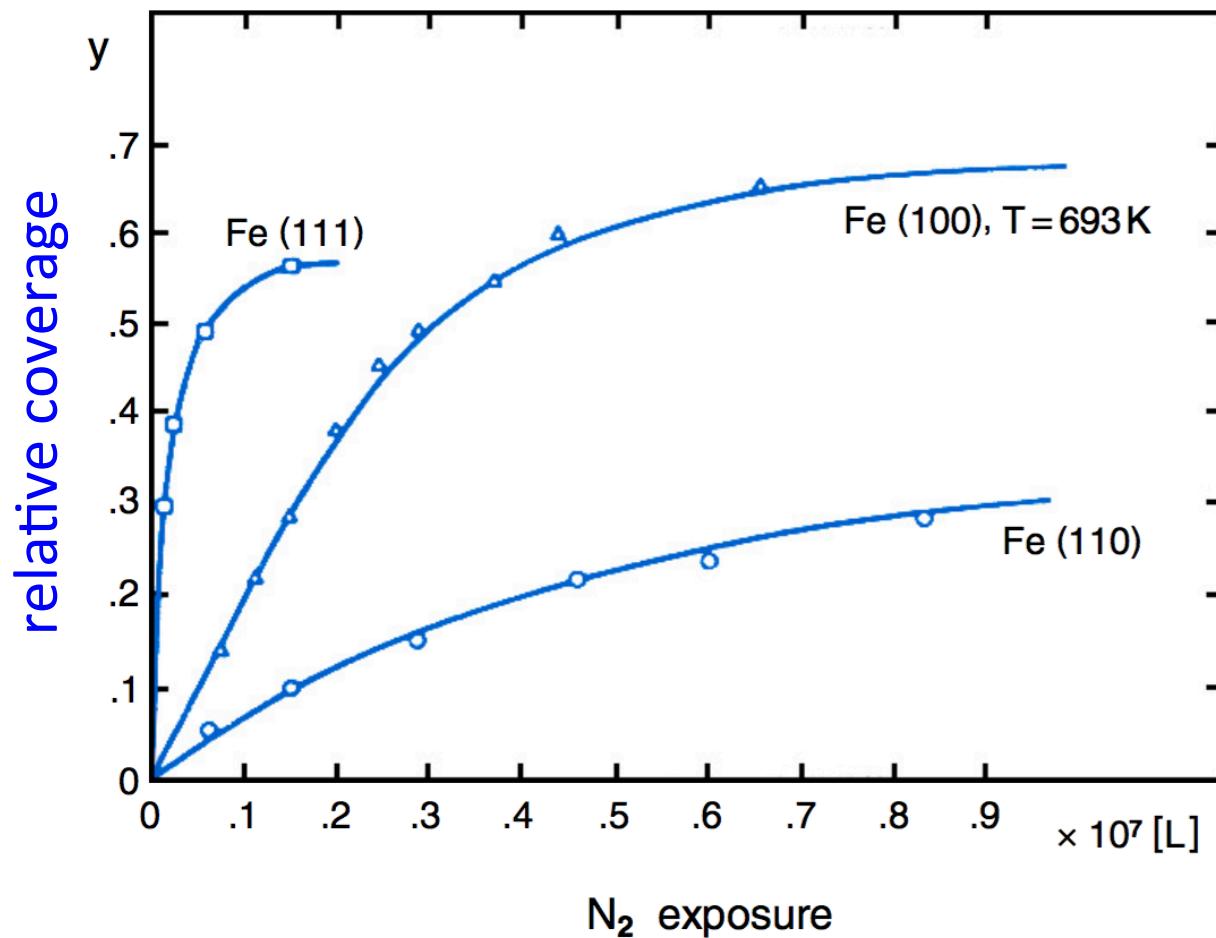
Fe (110)



Fe (100)



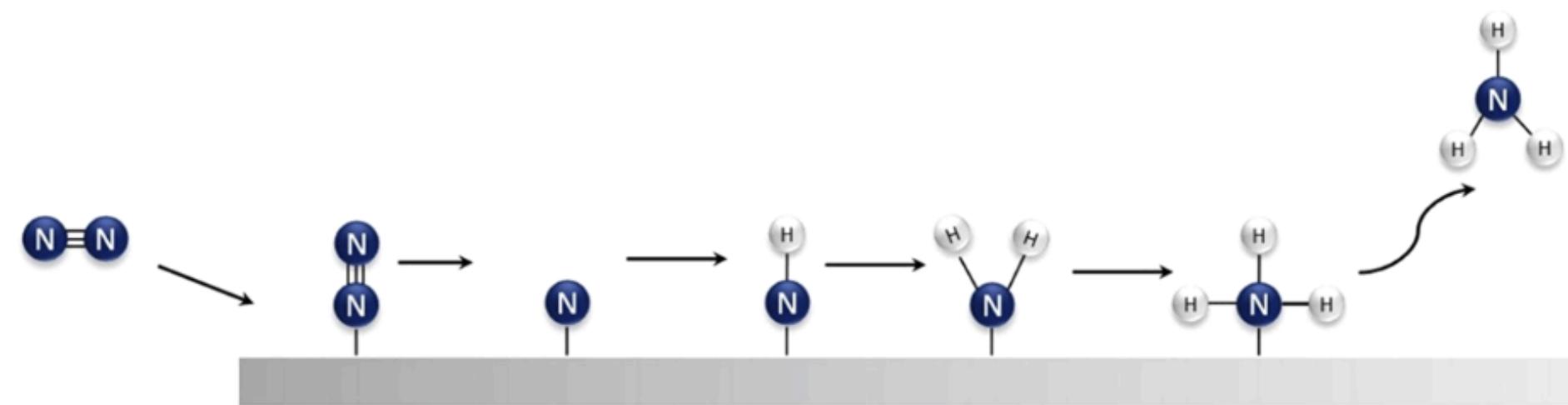
Fe (111)



There is a pronounced influence of the surface structure: The most densely packed (110) surface is least active, while the open (111) plane exhibits the highest sticking coefficient and is indeed also responsible for the overall activity of the industrial catalyst.

-- Relevant elementary reaction steps are:

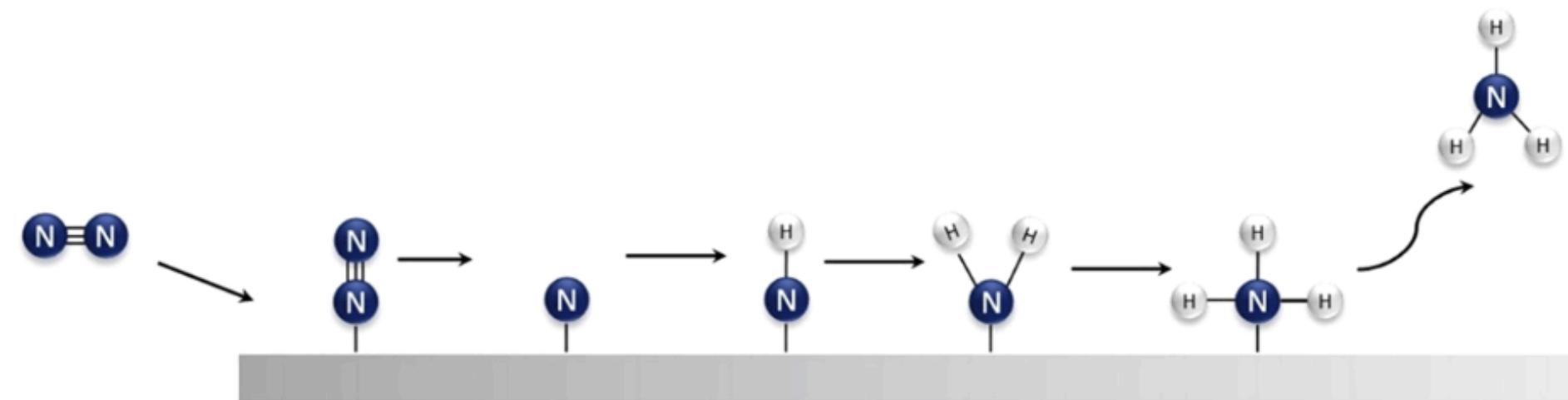
N₂ dissociation, H₂ dissociation, and hydrogenation of the intermediate reactants.



-- Relevant elementary reaction steps are:

N₂ dissociation, H₂ dissociation, and hydrogenation of the intermediate reactants.

-- Langmuir-Hinshelwood (LH) mechanism: In this both the reactants are dissociatively adsorbed on a surface before any reaction between their fragments takes place.

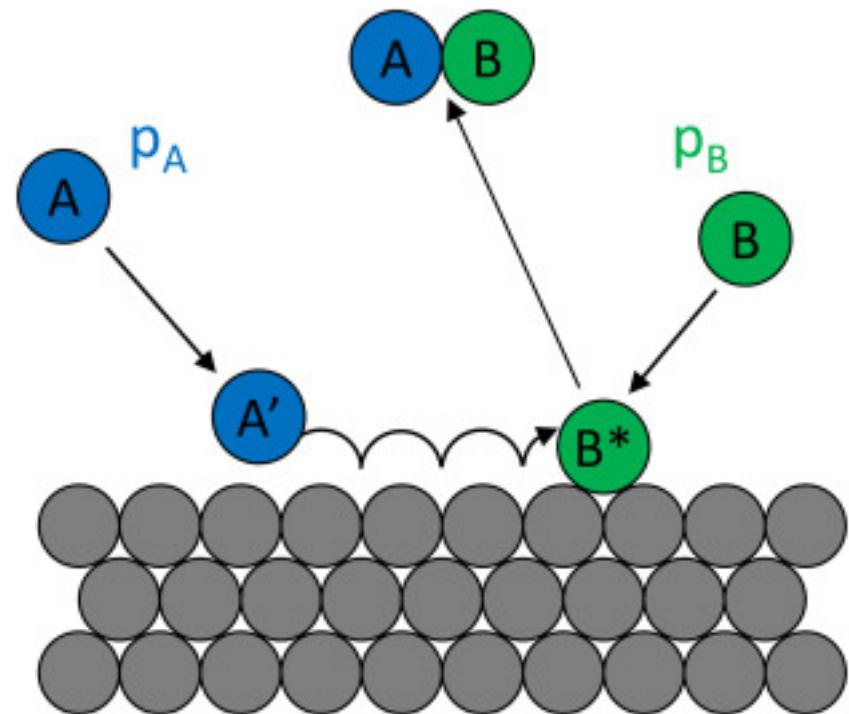


-- Langmuir-Hinshelwood (LH) mechanism: Schematic representation

In this both the reactants are dissociatively adsorbed on a surface before any reaction between their fragments takes place.

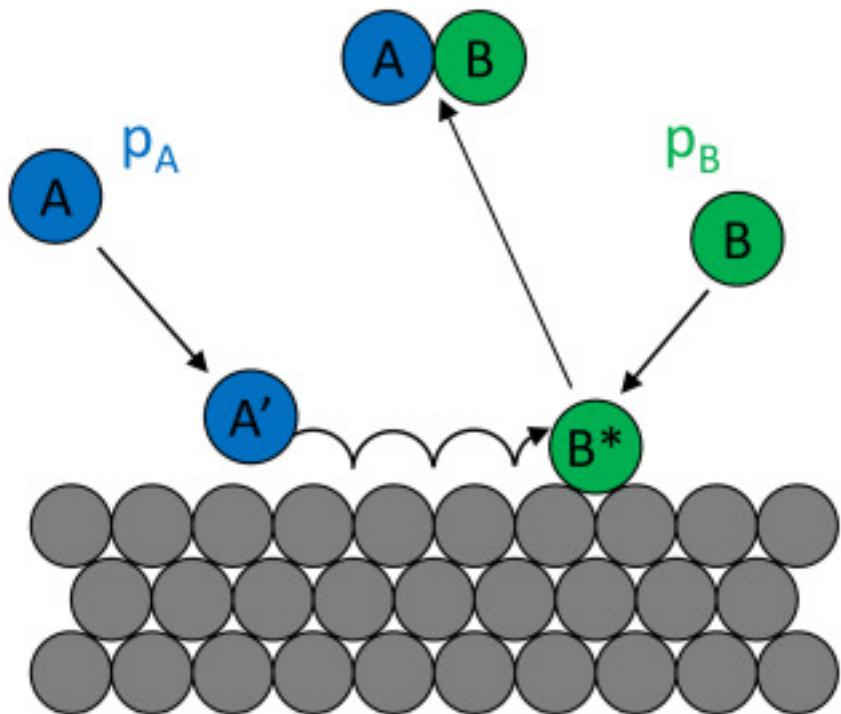
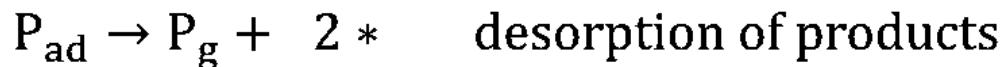
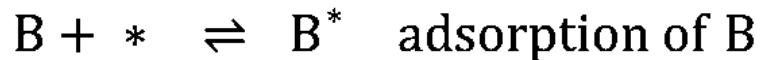
-- This mechanism assumes a bimolecular reaction involving two adjacent molecules on the surface, which are both adsorbed.

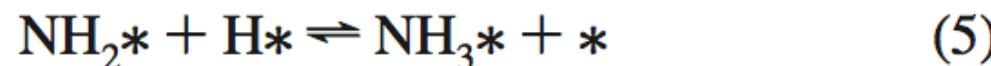
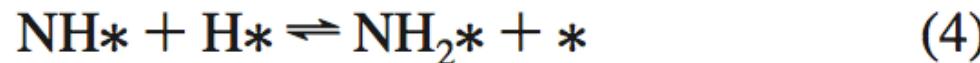
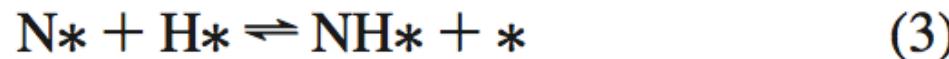
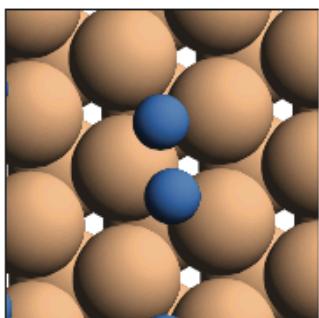
It is, furthermore, assumed that after the reaction, the product will leave the surface (desorb).



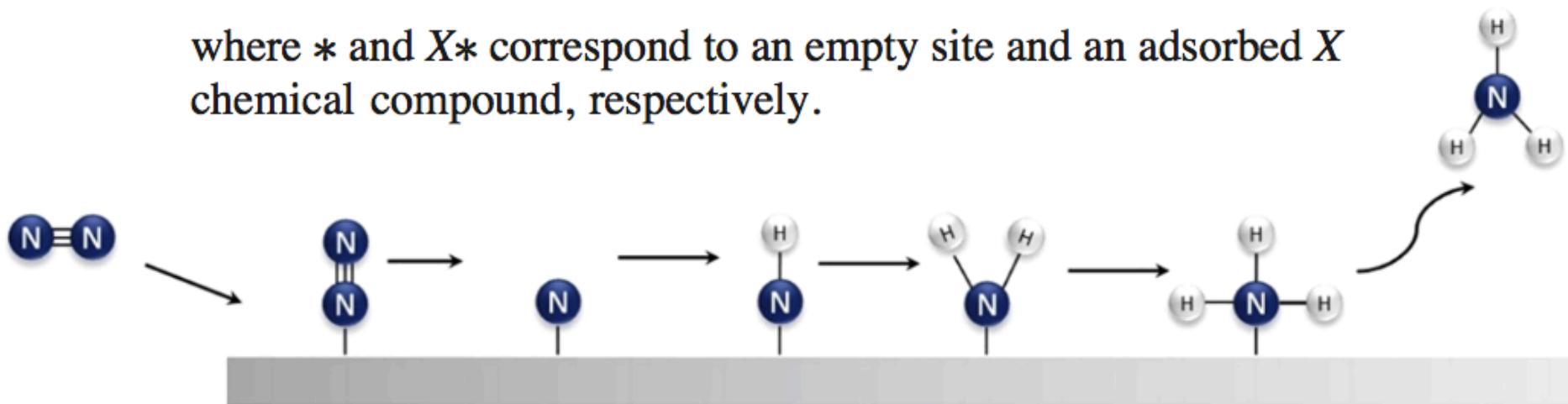
-- Langmuir-Hinshelwood (LH) mechanism: Schematic representation
In this both the reactants are dissociatively adsorbed on a surface before any reaction between their fragments takes place.

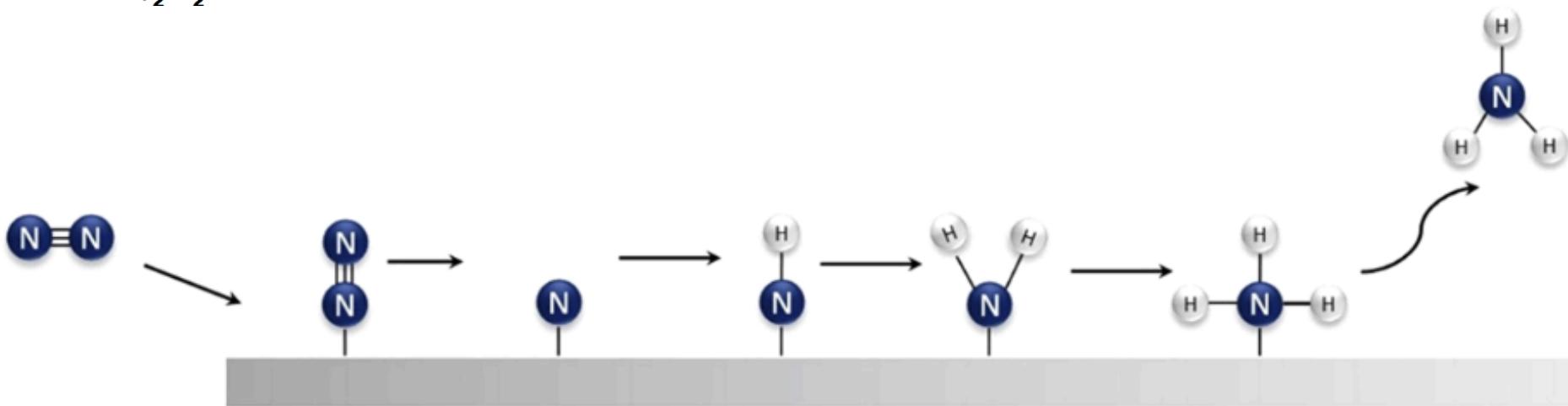
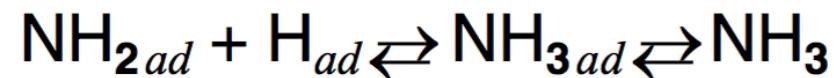
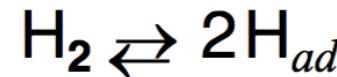
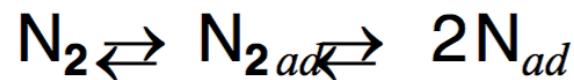
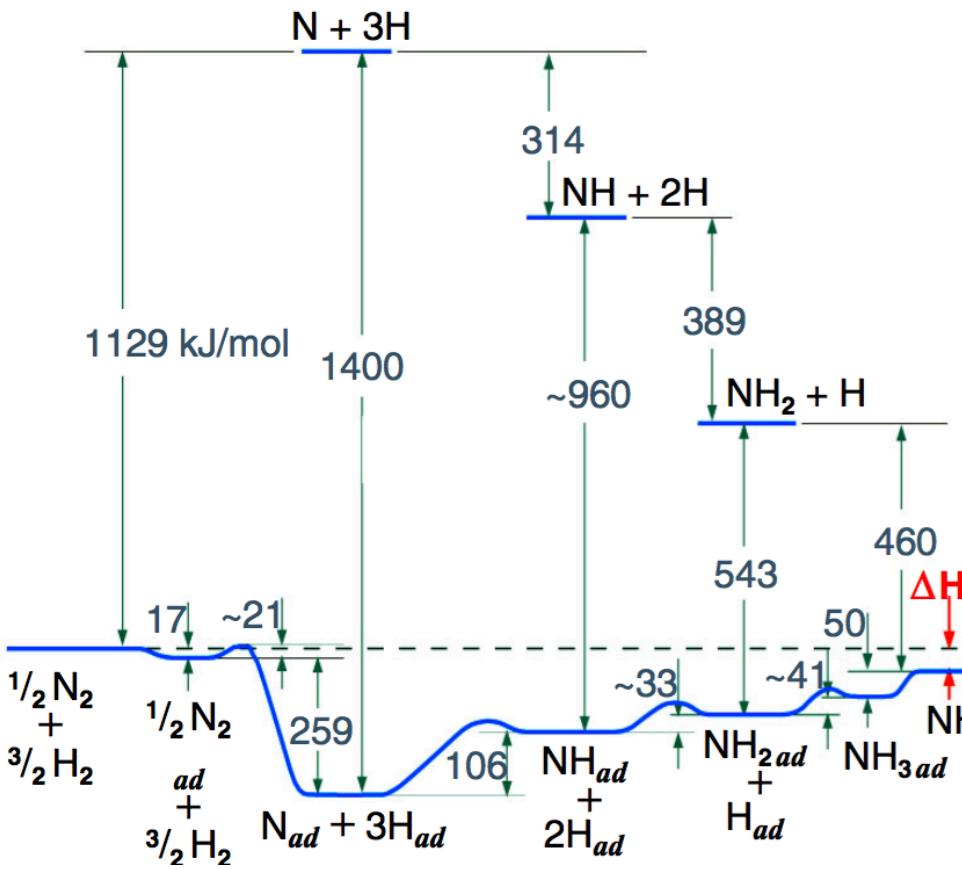
The involved processes can easily be described by a set of reaction equations, in which * designates adsorption sites on the surface.





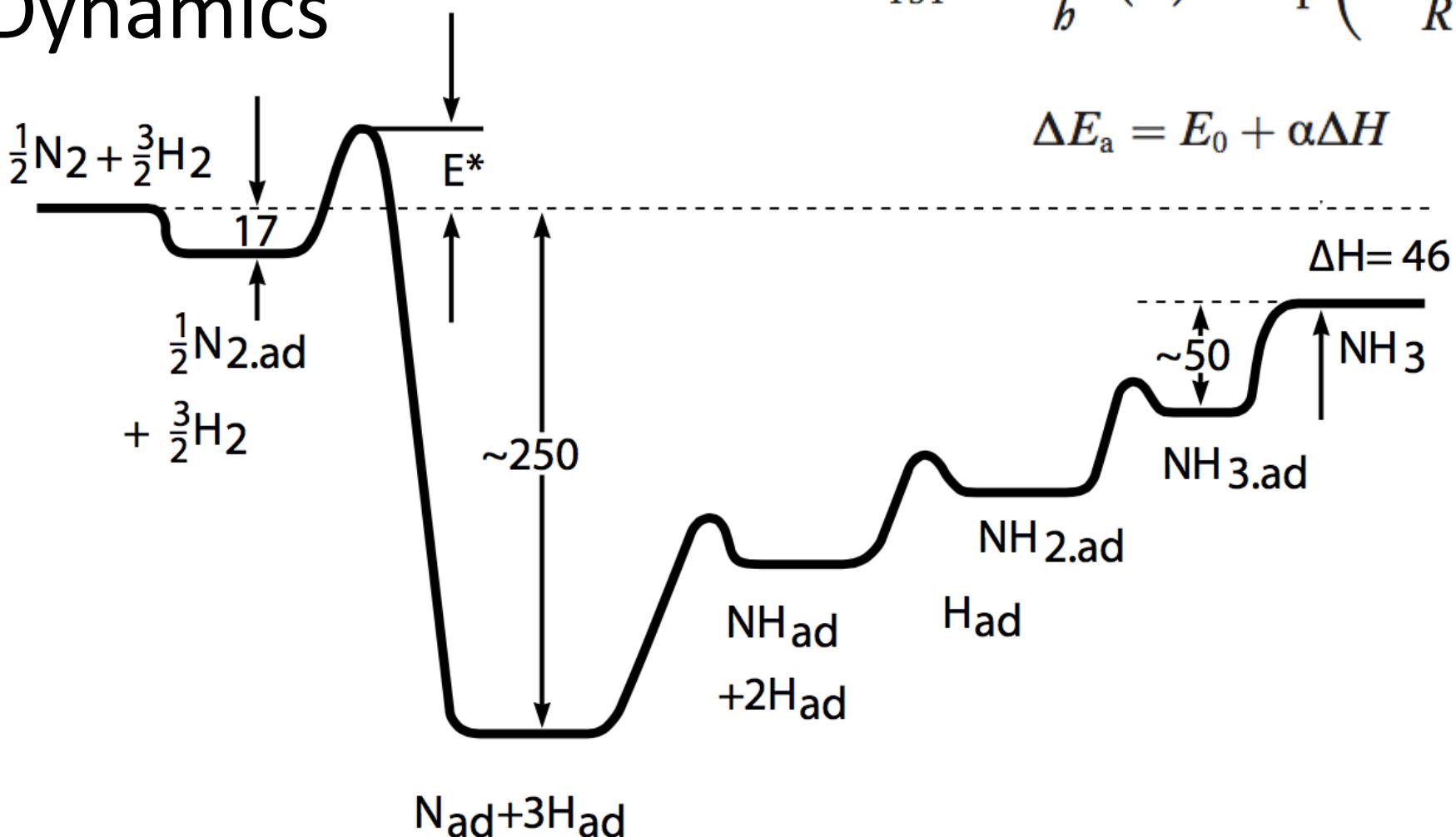
where $*$ and $X*$ correspond to an empty site and an adsorbed X chemical compound, respectively.





Chemical Reaction Dynamics

$$k_{\text{TST}} = \frac{k_{\text{B}} T}{b} (c^{\circ})^{\Delta v^{\dagger}} \exp\left(-\frac{\Delta G^{\circ\dagger}}{RT}\right)$$



An energy diagram showing the progression of the reaction from the reactants N_2 and H_2 to the product NH_3 . Energies are given in units of kJ/mol. (Adapted from Ertl 1983)

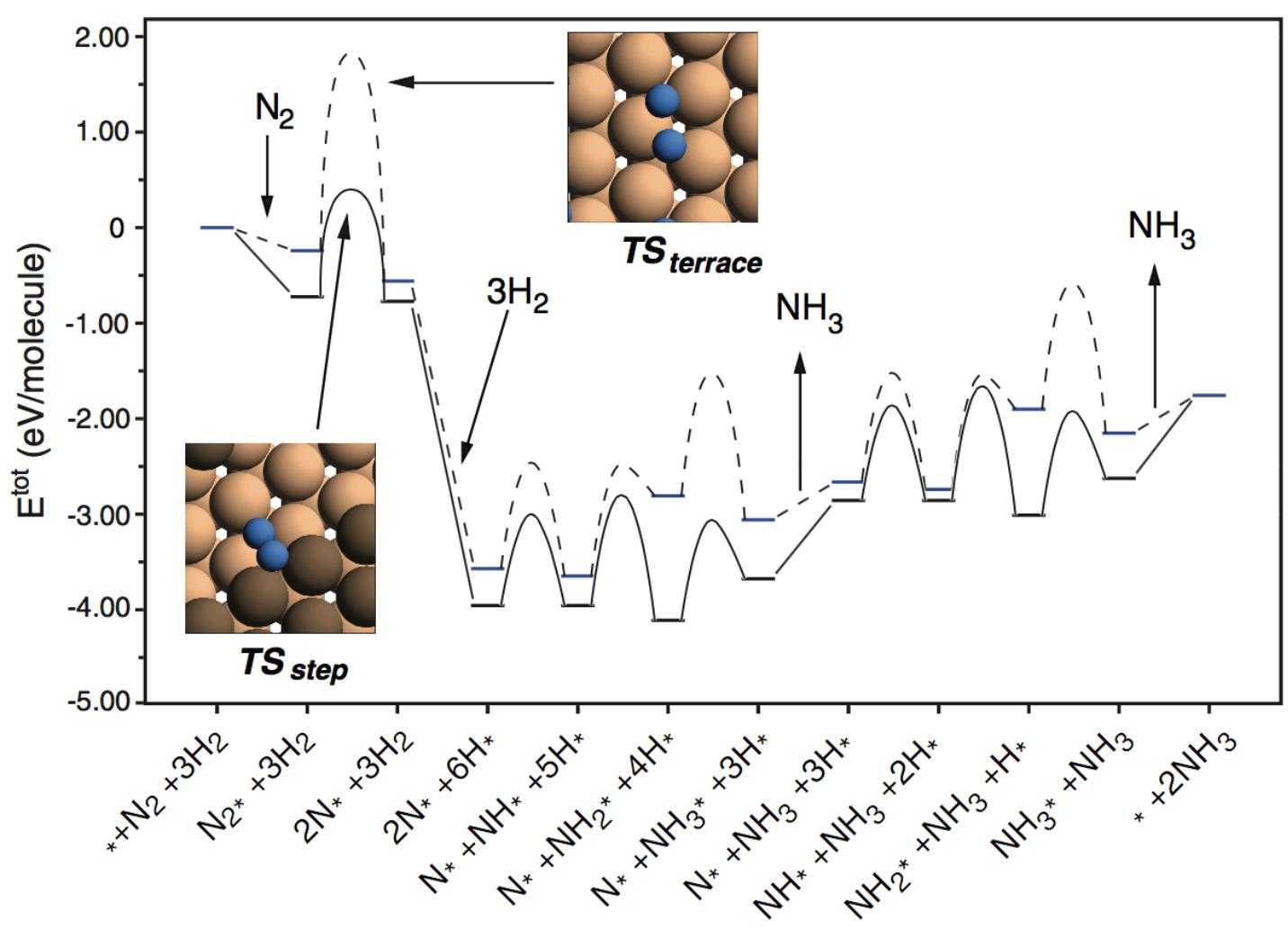
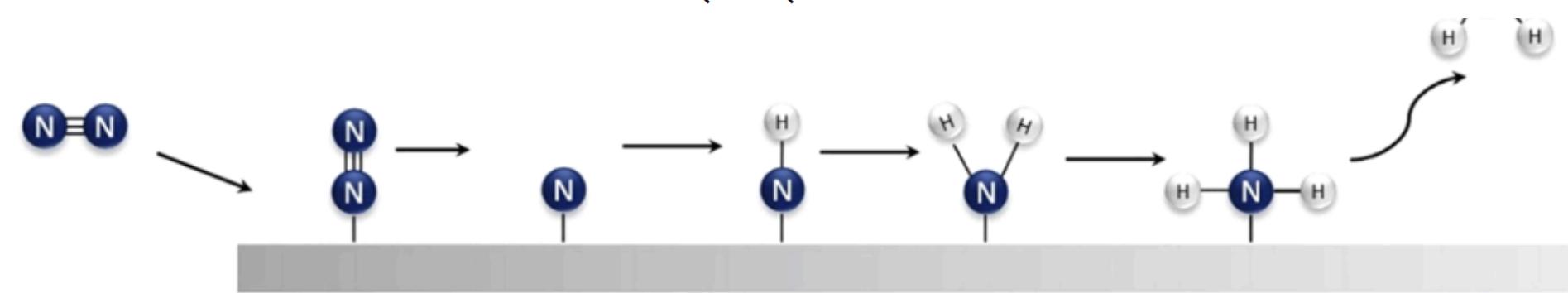
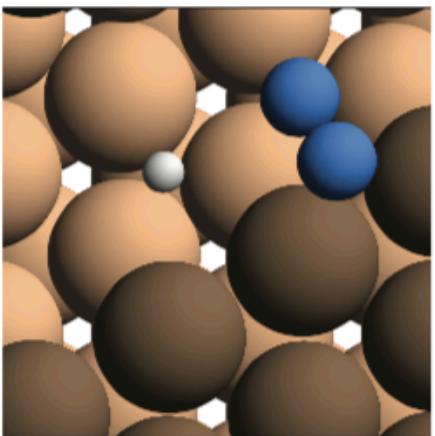
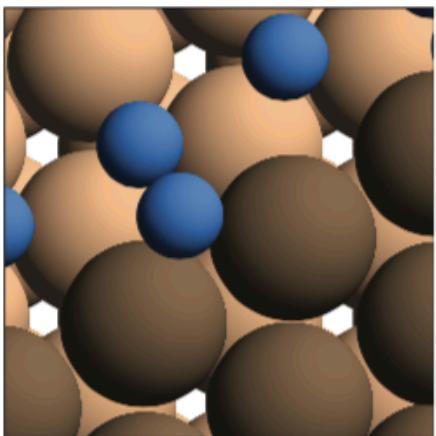
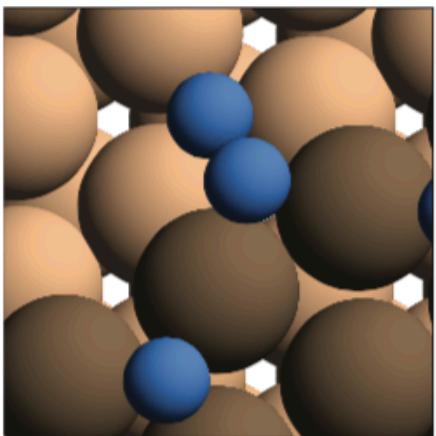
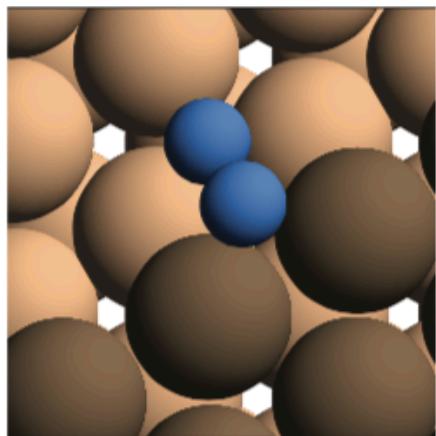


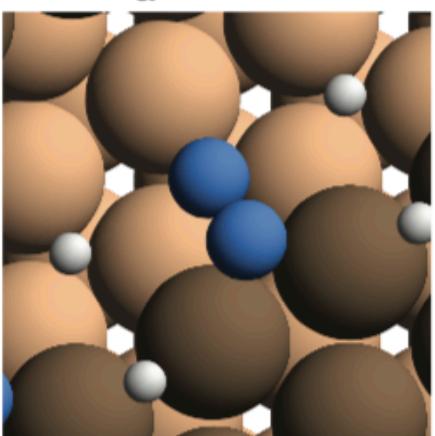
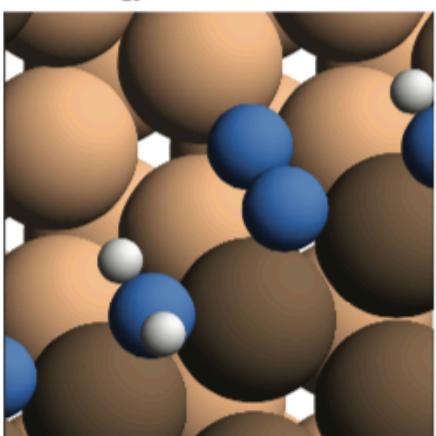
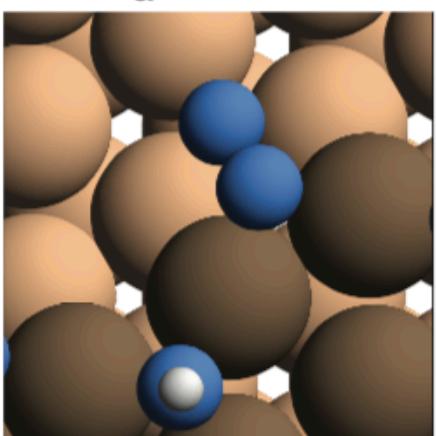
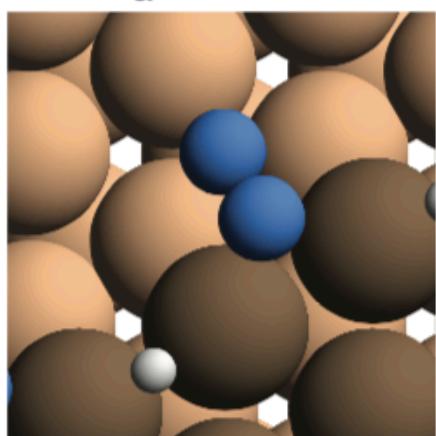
Fig. 1. The calculated potential energy (E^{tot}) diagram for NH_3 synthesis from N_2 and H_2 over close-packed (001) and stepped Ru surfaces (20). A * denotes an empty site and X^* an adsorbed species. The configuration of the transition states (TS) for N_2 dissociation over the terrace and step sites is shown in the insets.

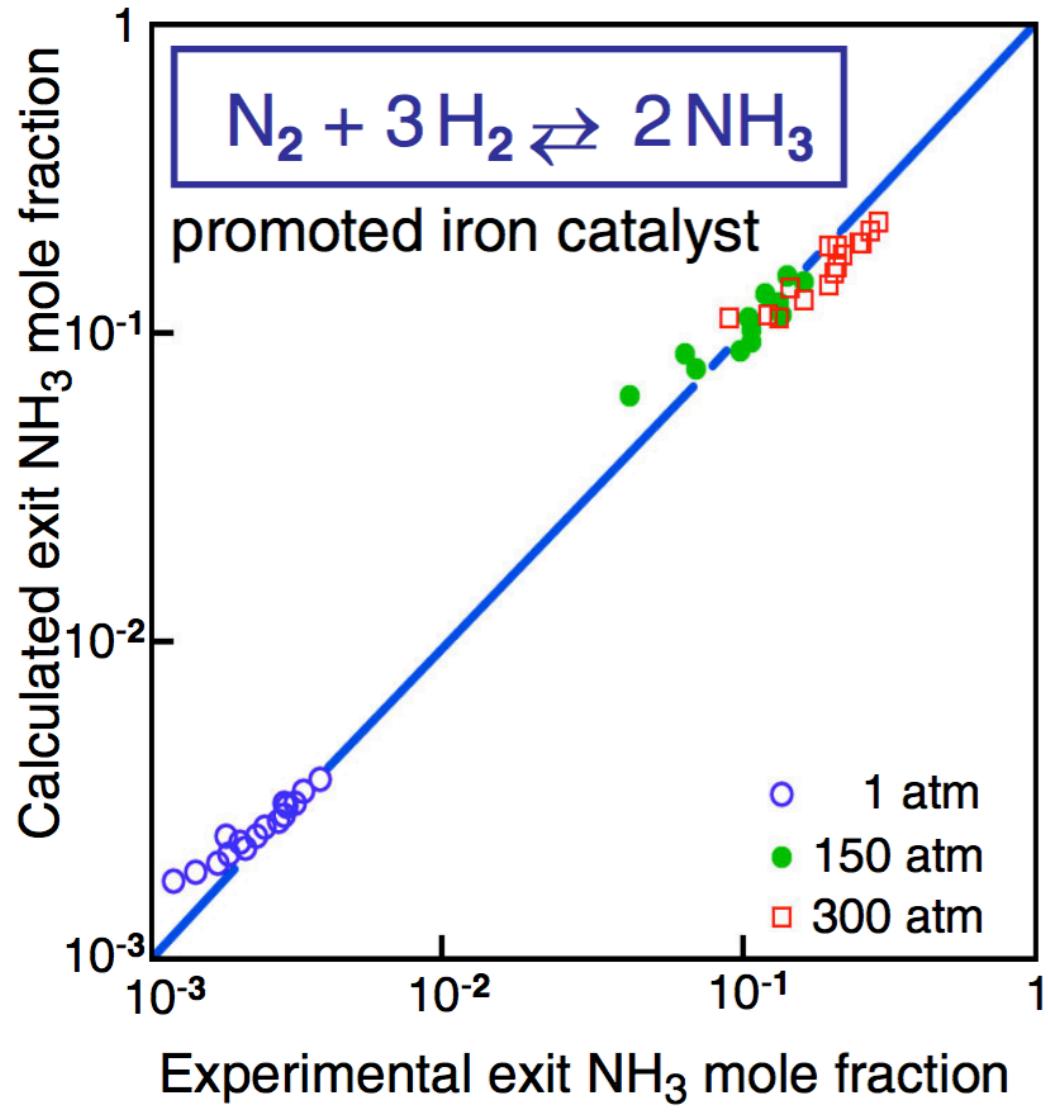


A $E_a=0.49$ eV **B** $E_a=0.57$ eV **C** $E_a=1.25$ eV **D** $E_a=0.81$ eV



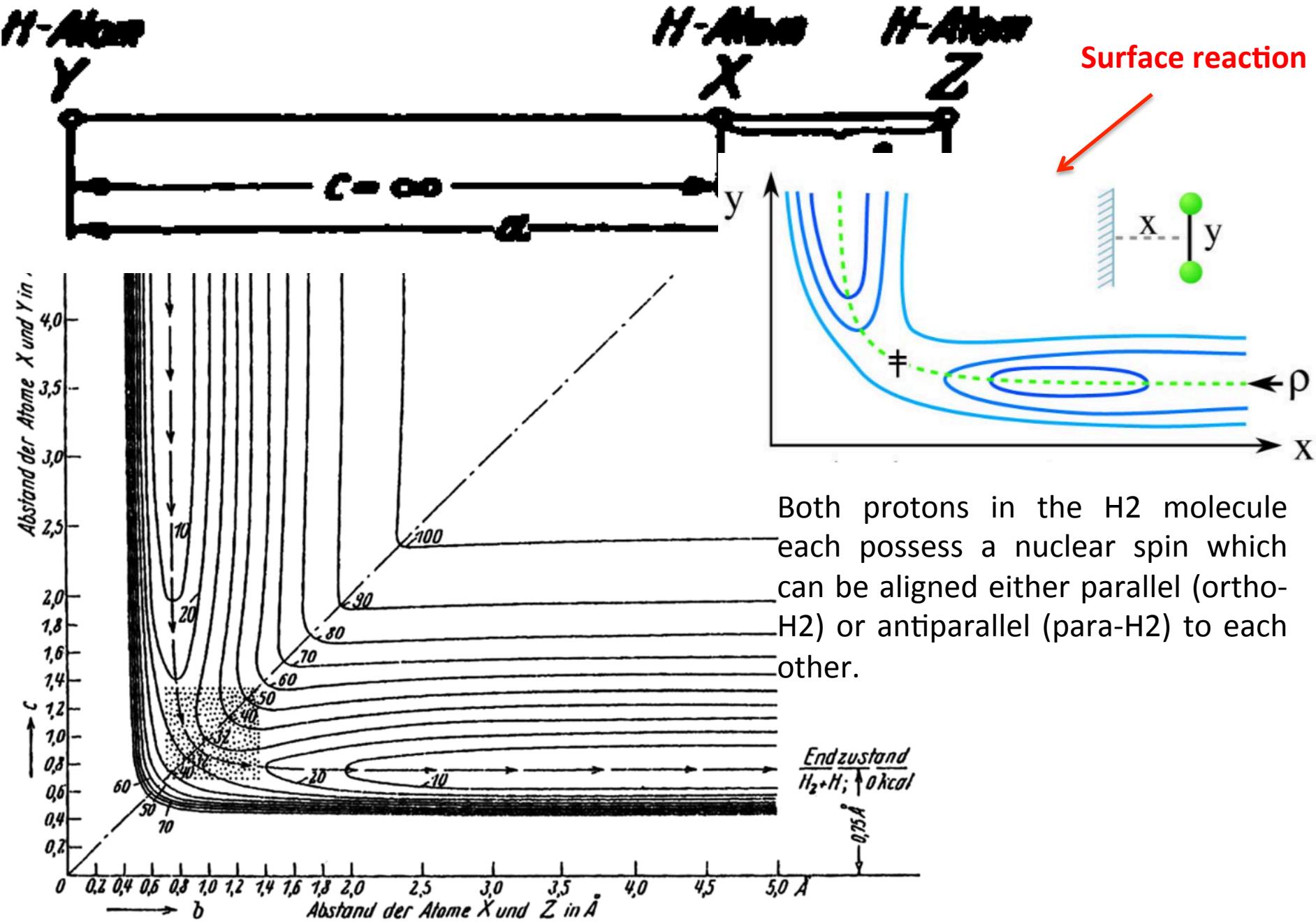
E $E_a=0.67$ eV **F** $E_a=0.71$ eV **G** $E_a=1.06$ eV **H** $E_a=0.99$ eV

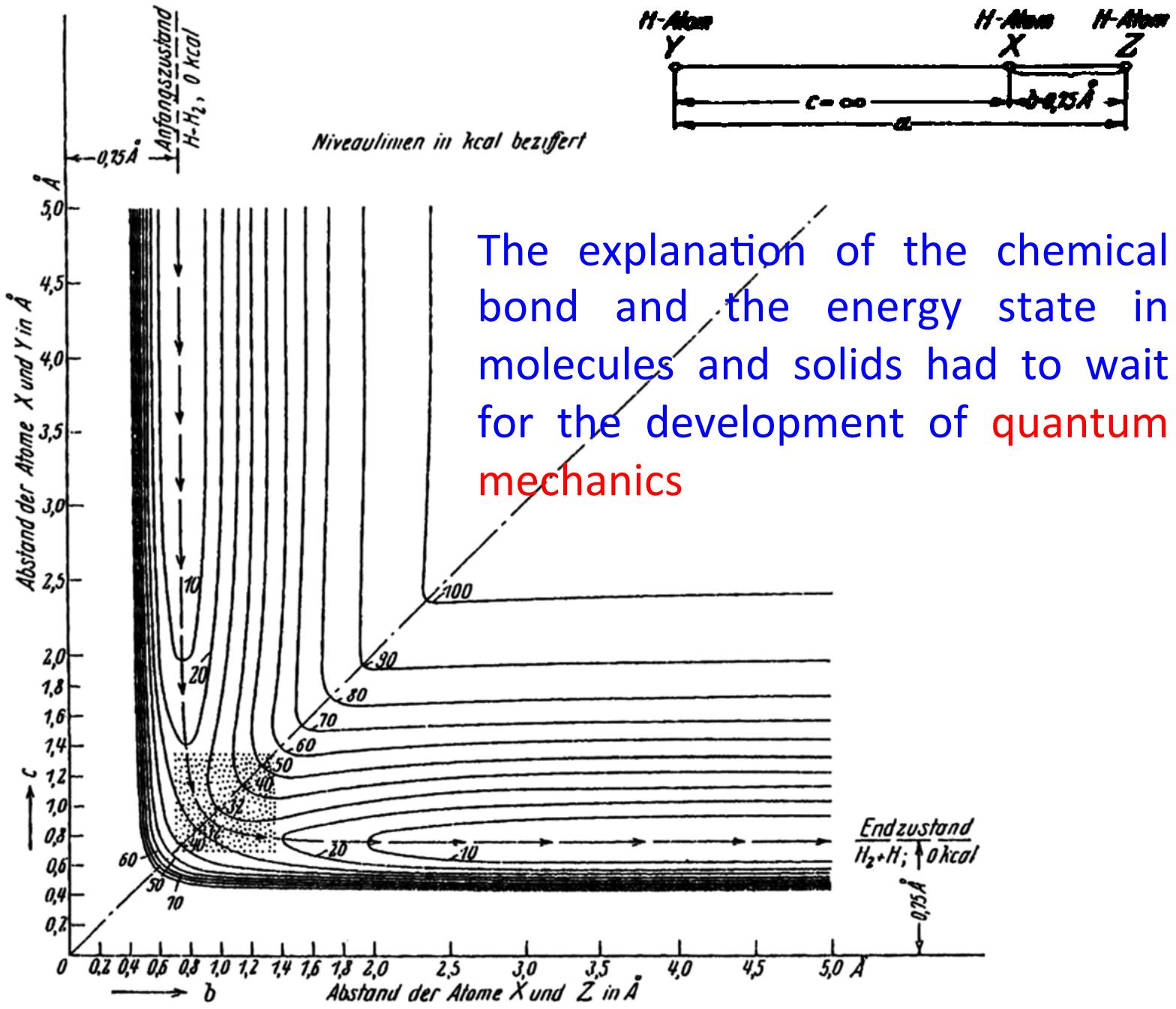




The data points barely deviate from the straight line which marks **complete agreement between theory and experiment**.

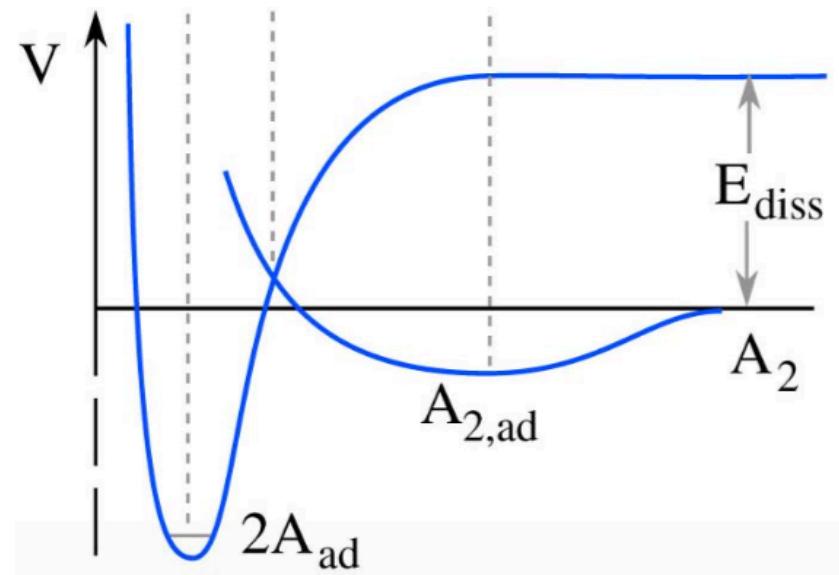
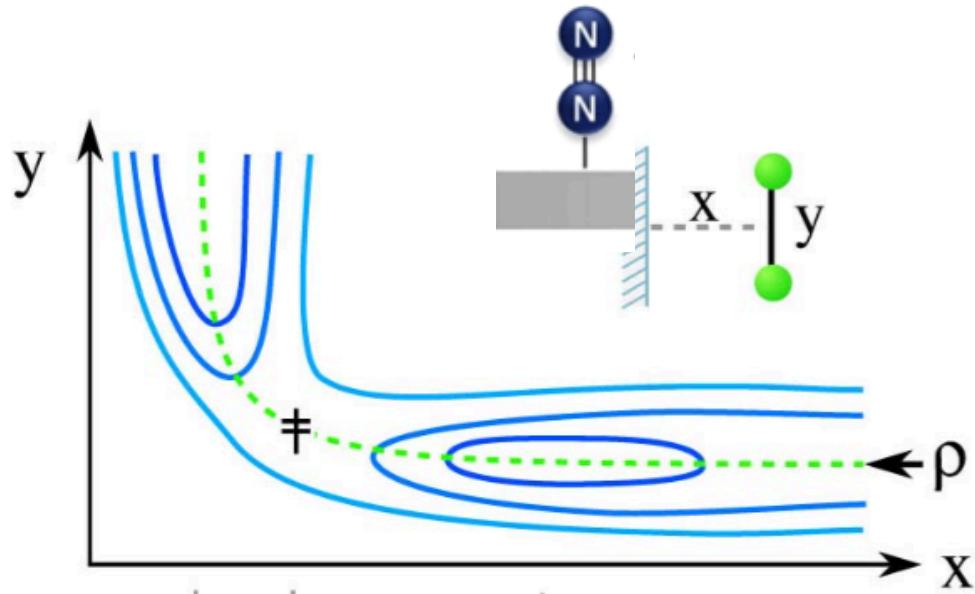
calculation of the theoretical energy of the simplest reaction, the linear conversion $H + H_2 \rightarrow H_2 + H$ as a function of both relevant distances (Figure 15) followed after the development of quantum mechanics, and consequently the formulation of the theory of the transition state by Henry Eyring and Michael Polanyi,^[22] also at the KWI for Physical Chemistry, Berlin. On the basis of this theory, the fruitful area of reaction dynamics was developed, in which enormous progress could be made in understanding elementary chemical reactions both experimentally (e.g. by molecular beam and laser techniques) and also theoretically.





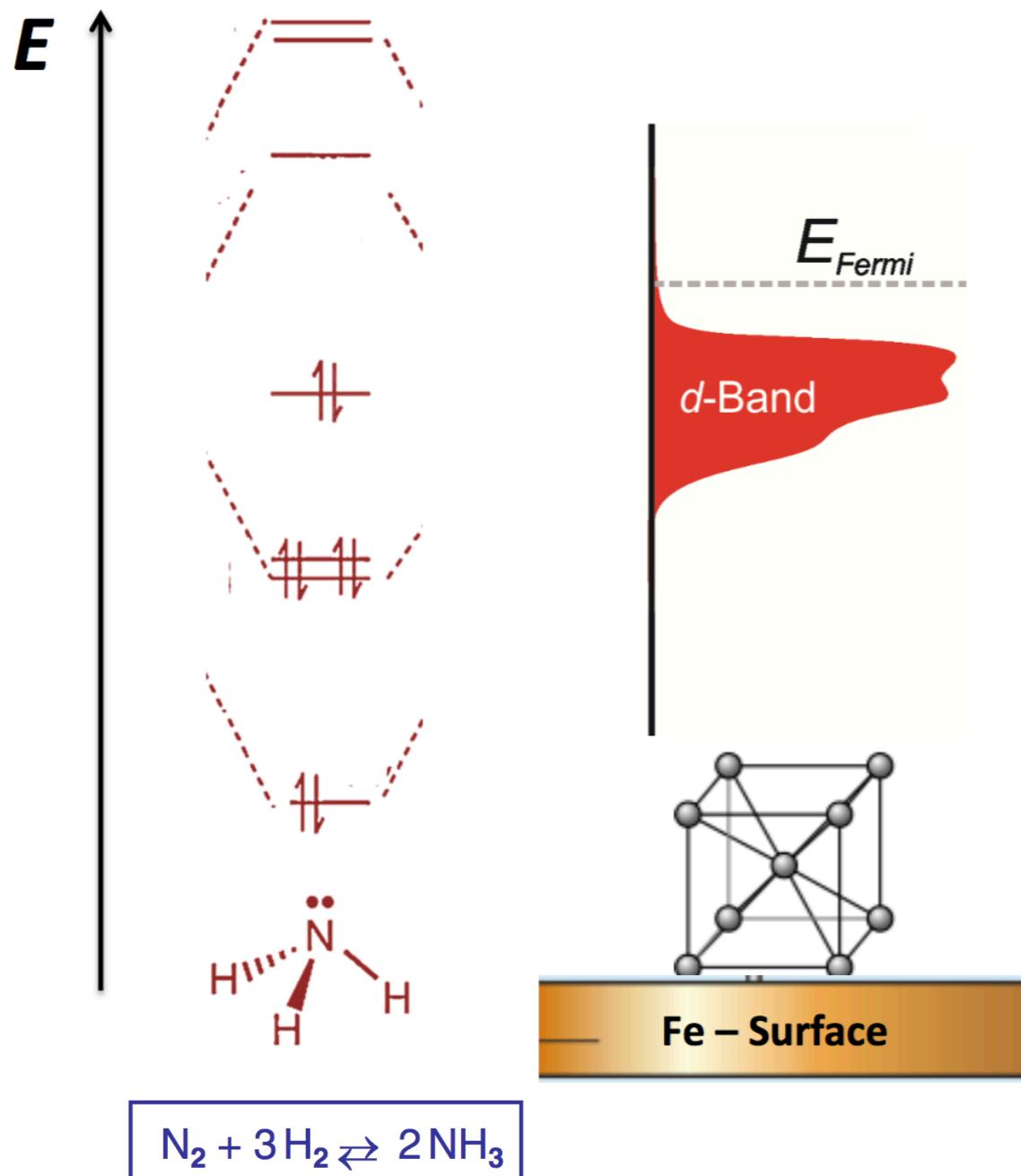
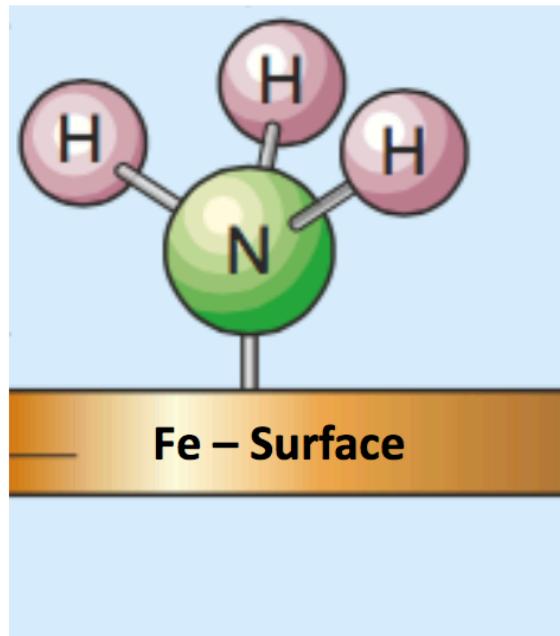
The explanation of the chemical bond and the energy state in molecules and solids had to wait for the development of quantum mechanics

Hypersurface potential for the reaction $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ as a function of both distances b and c according to Eyring and Polanyi.

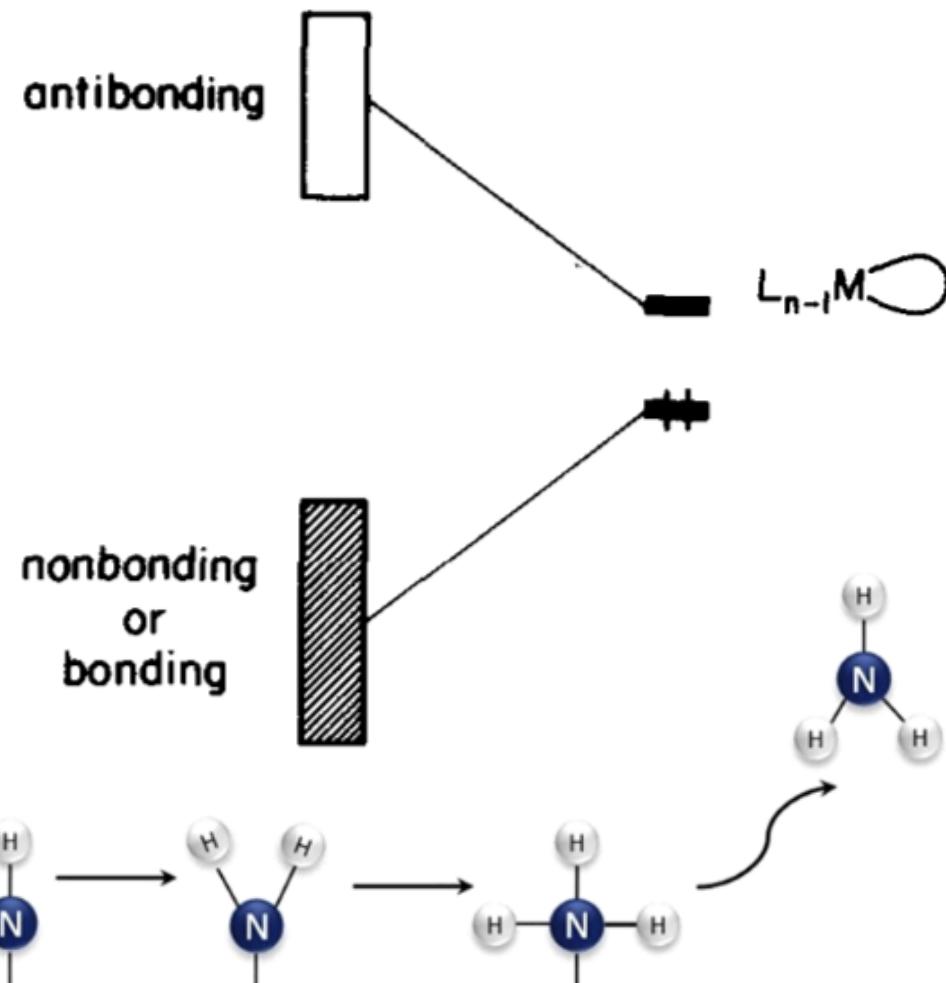
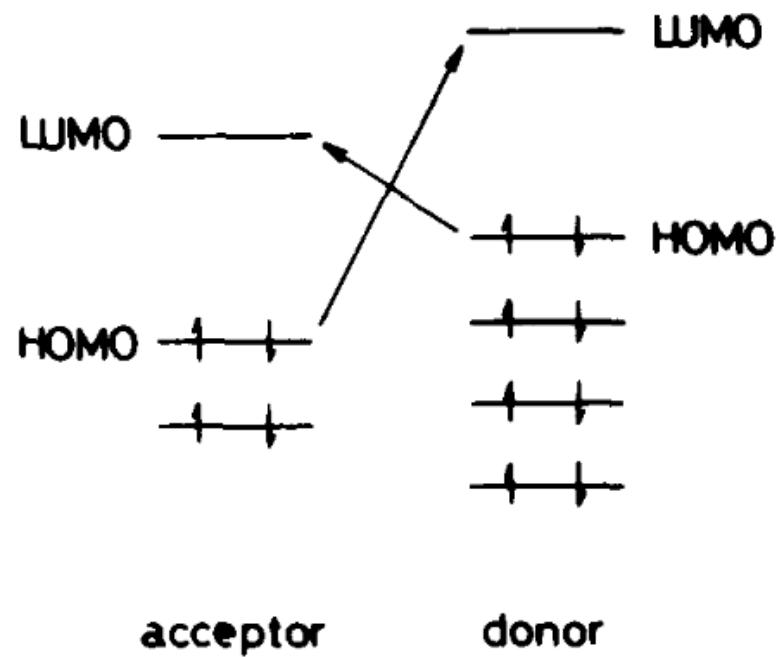


“The explanation of the chemical bond and the energy state in molecules and solids had to wait for the development of quantum mechanics”

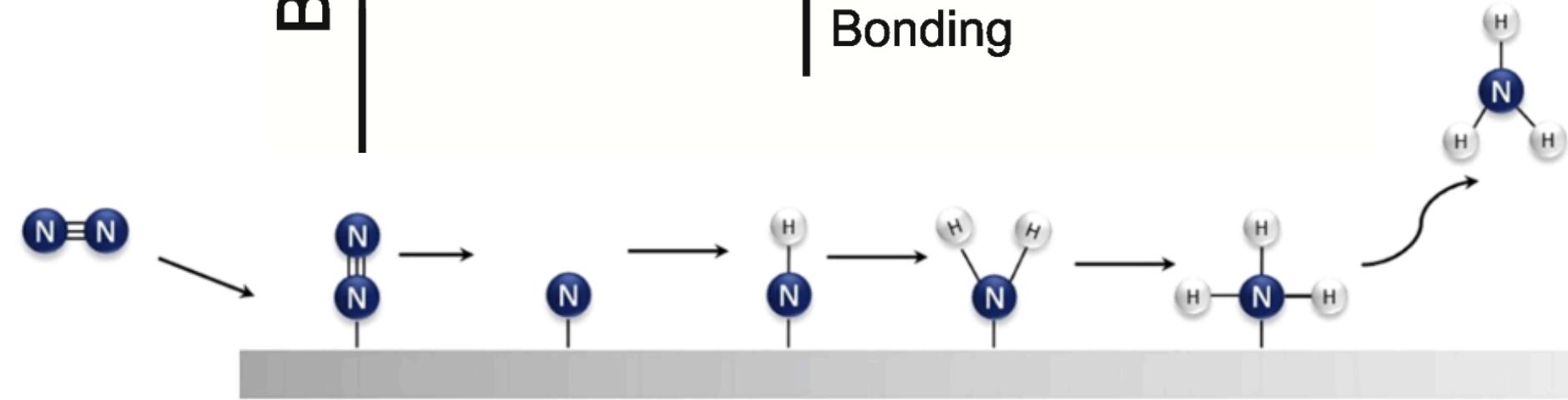
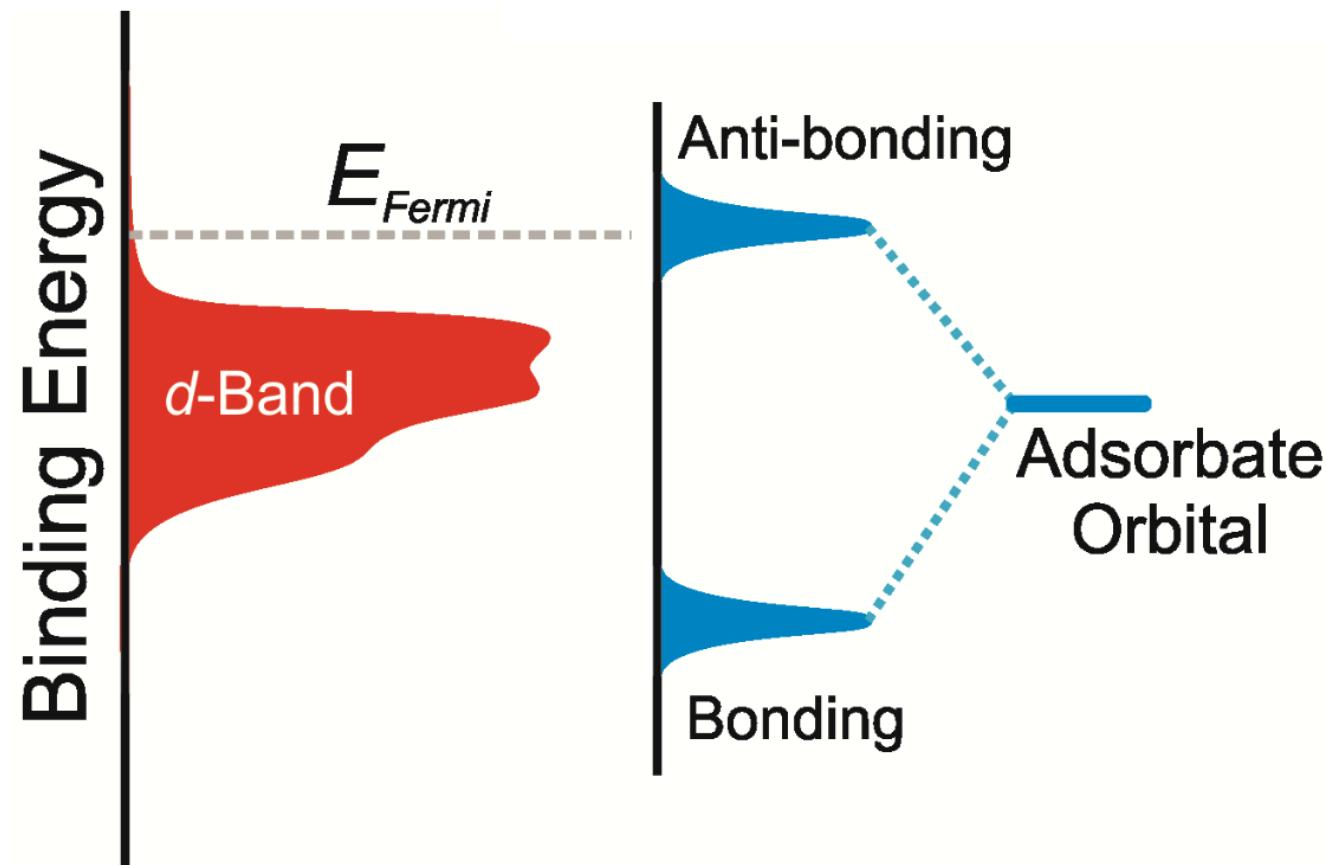
Chemical processes on solid surfaces

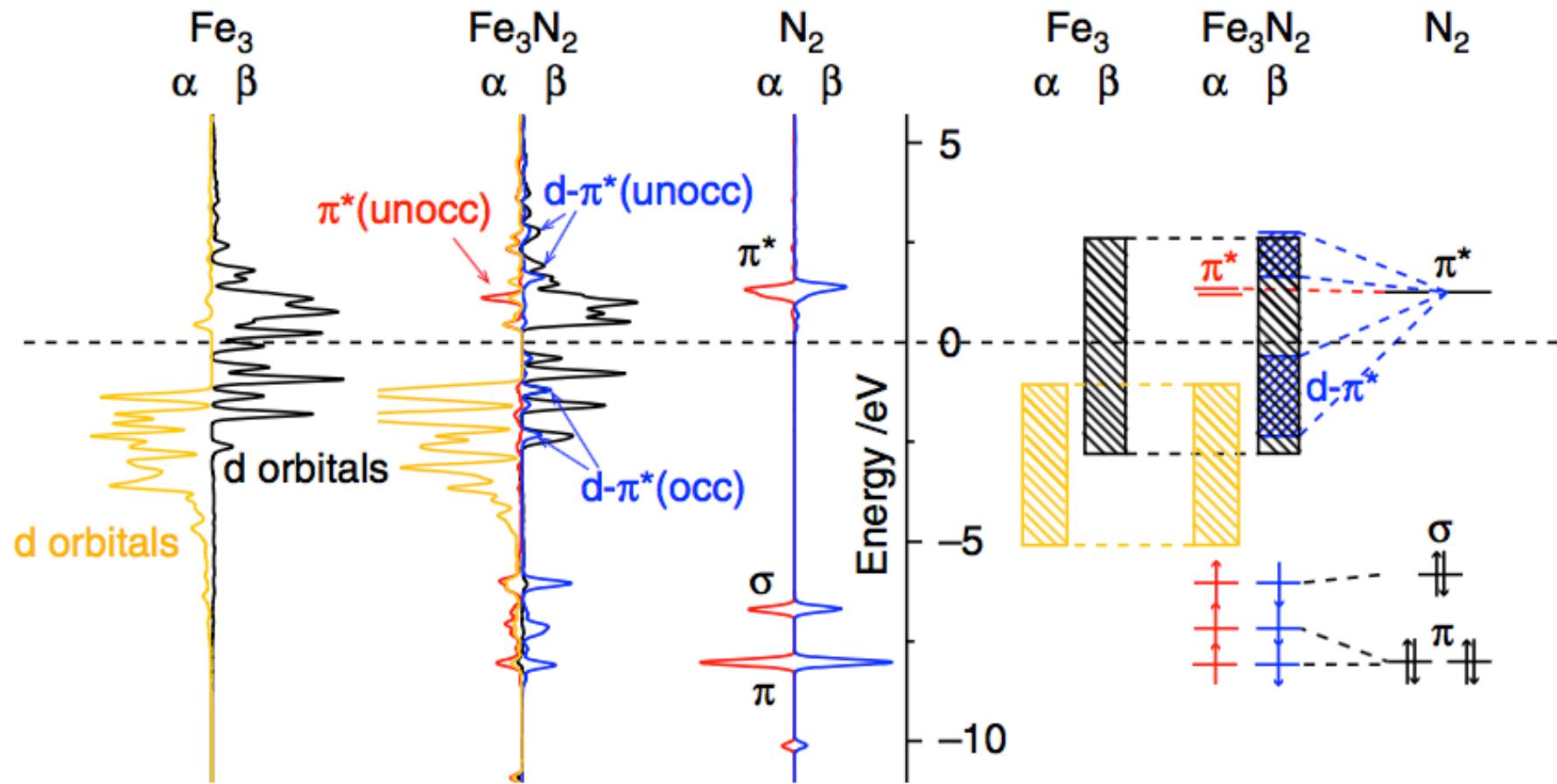


Frontier Orbitals in Chemical Reactions



Frontier Orbitals in Chemical Reactions



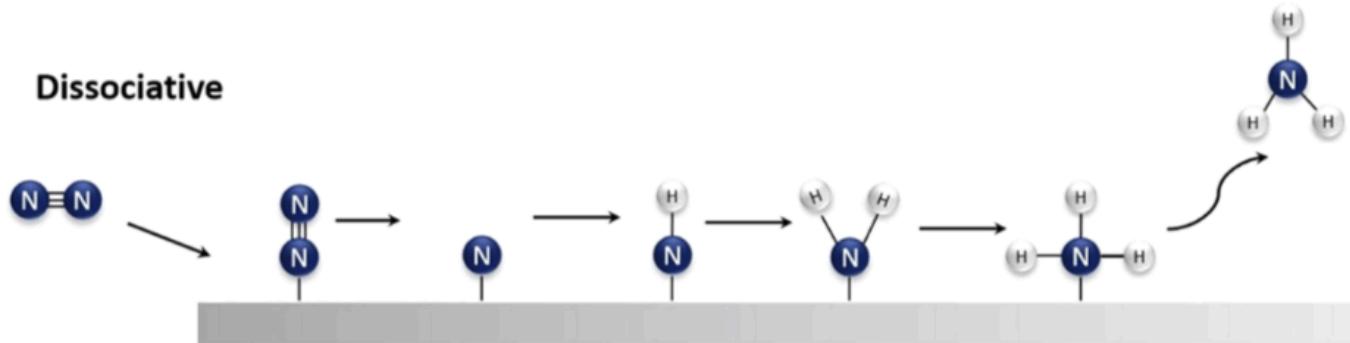


is required. It is currently accepted that N_2 reduction in the HB process occurs through a dissociative mechanism,⁶ wherein the N–N bond is severed first and adsorbed atomic N is then reduced. However, identification of several intermediates in nitrogenase^{7,8} has suggested that the mechanism in diazotrophs, or electrochemical systems in general, might follow an associative mechanism wherein molecular N_2 reduction is followed by eventual N–N bond splitting. These two mechanisms are illustrated in Fig. 1.

Theoretical studies have used the scaling and presumed Brønsted–Evans–Polanyi (BEP) relationships for dissociative and associative mechanisms to propose a volcano relationship and predict the optimum N_2 electroreduction catalyst.^{9,10} For late transition metal catalysts, the binding energy of NH_x ($x = 0, 1, 2$) species to transition metal surfaces correlates

a)

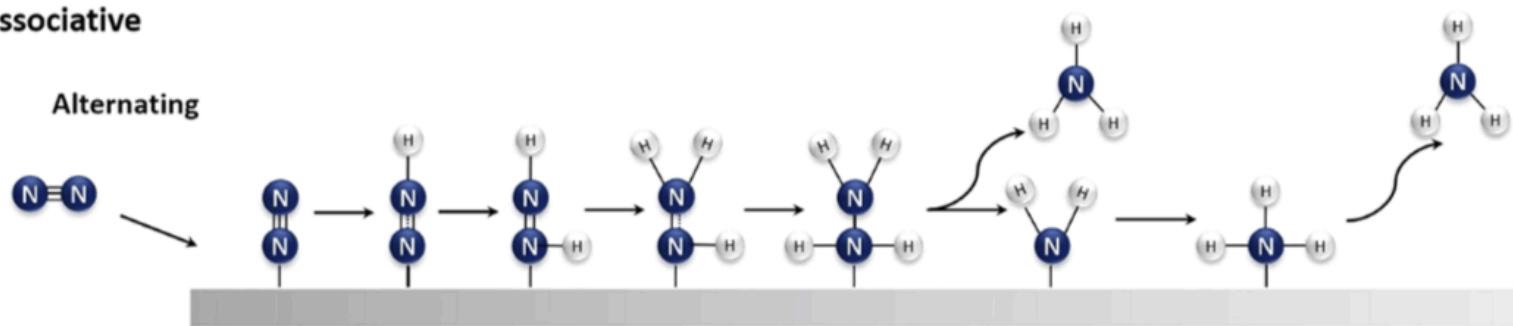
Dissociative



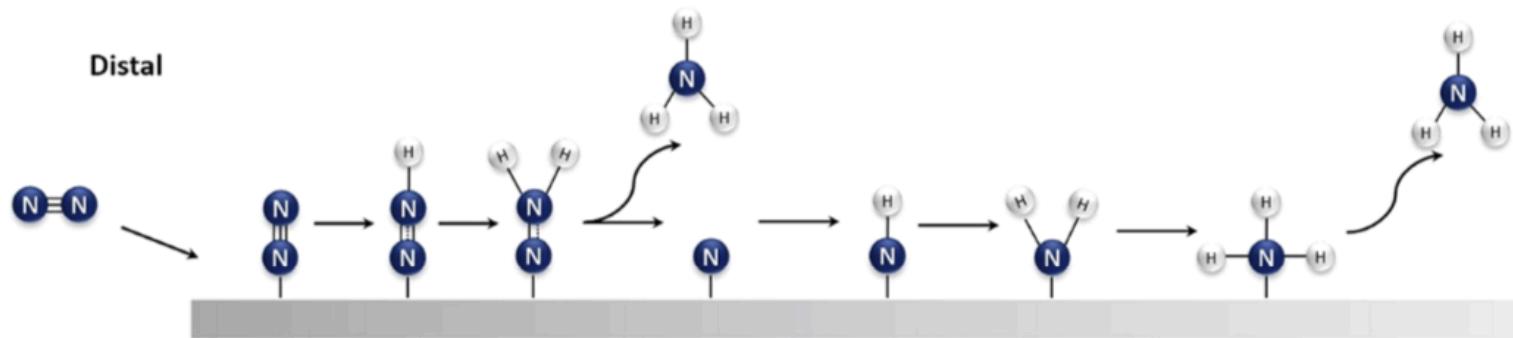
b)

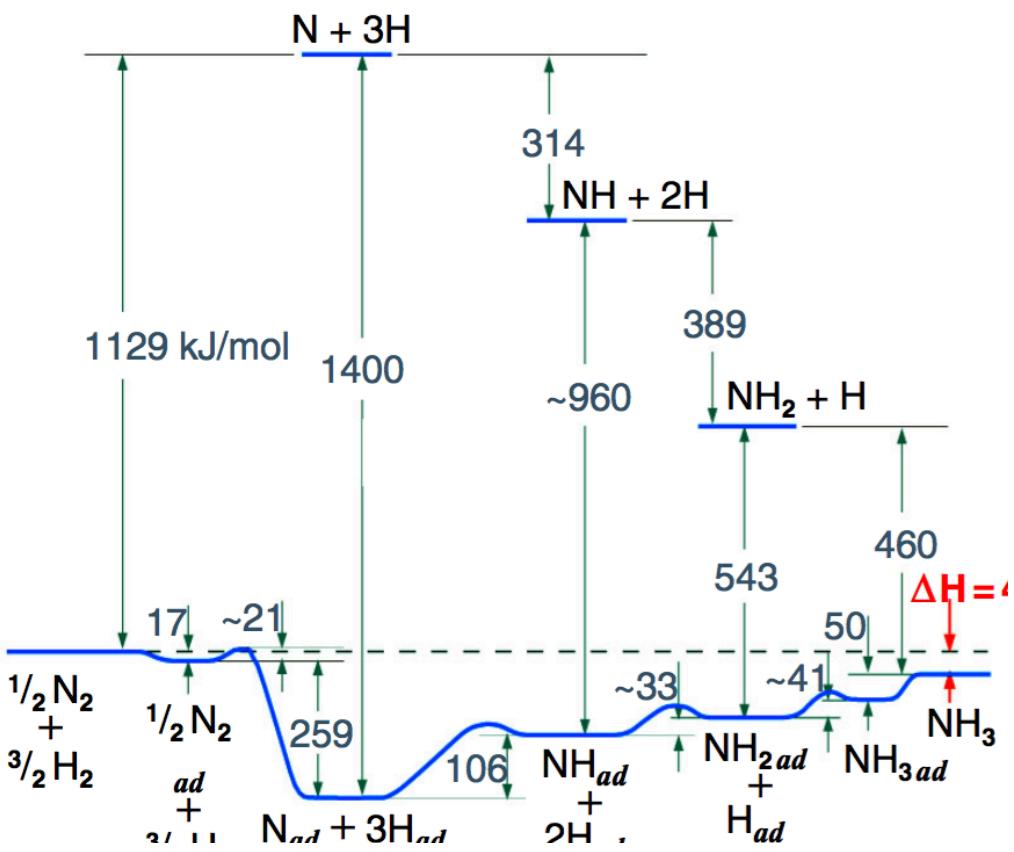
Associative

Alternating



Distal

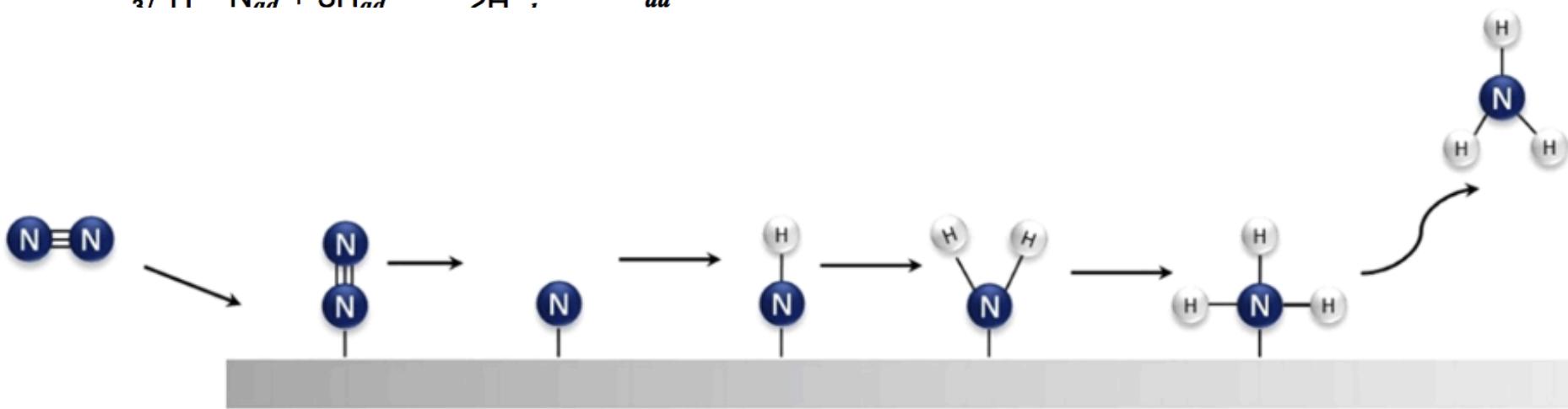




Using transition state theory, It has been shown that N_2 dissociation is by far the slowest step that is the rate limiting step.

The activation energy for dissociation, $E_{a,i}$, and thus the rate constant,

$$k = k_0 e^{-E^*/RT}$$



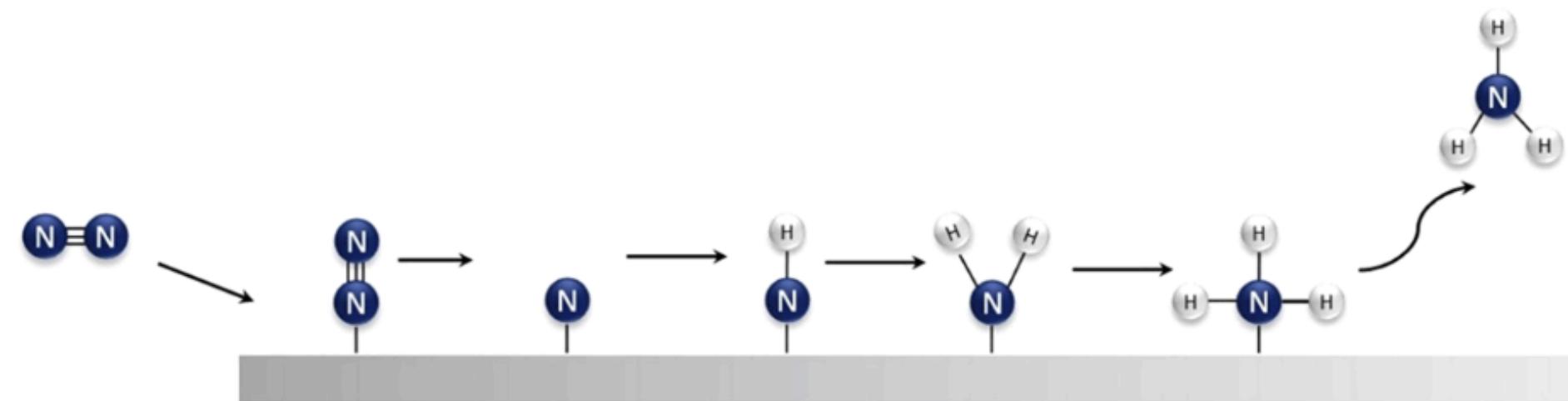
Catalytic activities have been correlated with various electronic properties of the catalyst, and it seems natural to relate the activity to bond energies.

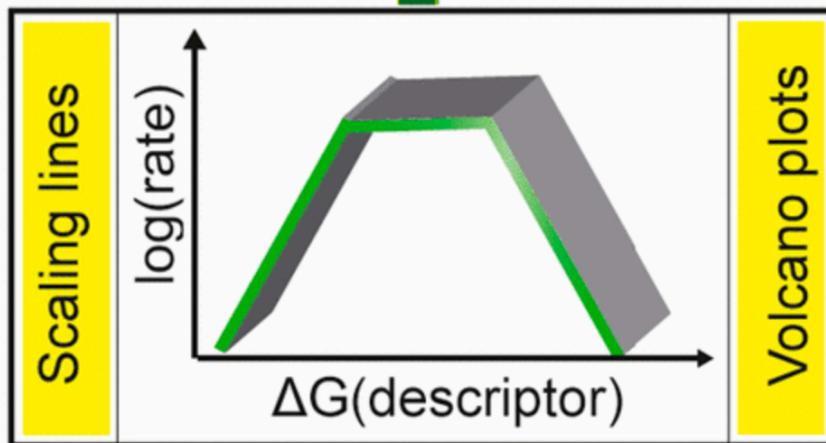
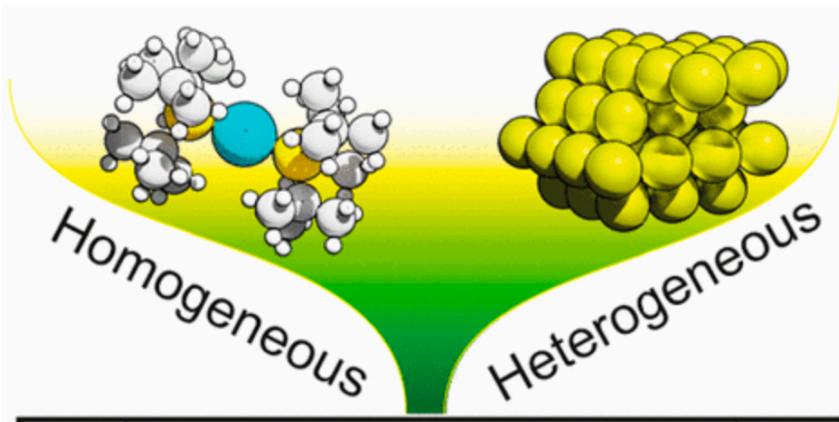
Using transition state theory, It has been shown that N₂ dissociation is by far the slowest step that is the rate limiting step.

The activation energy for dissociation, E_{a,i}, and thus the rate constant,

$$k = k_0 e^{-E^*/RT}$$

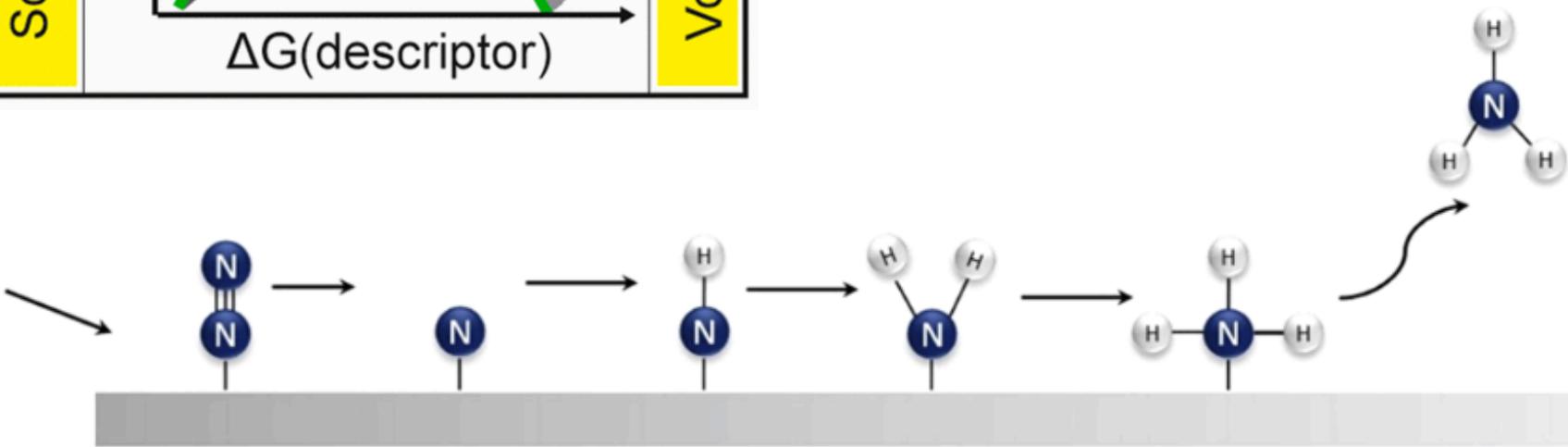
Interactions between the catalyst and the substrate should be "just right" – The Sabatier principle.

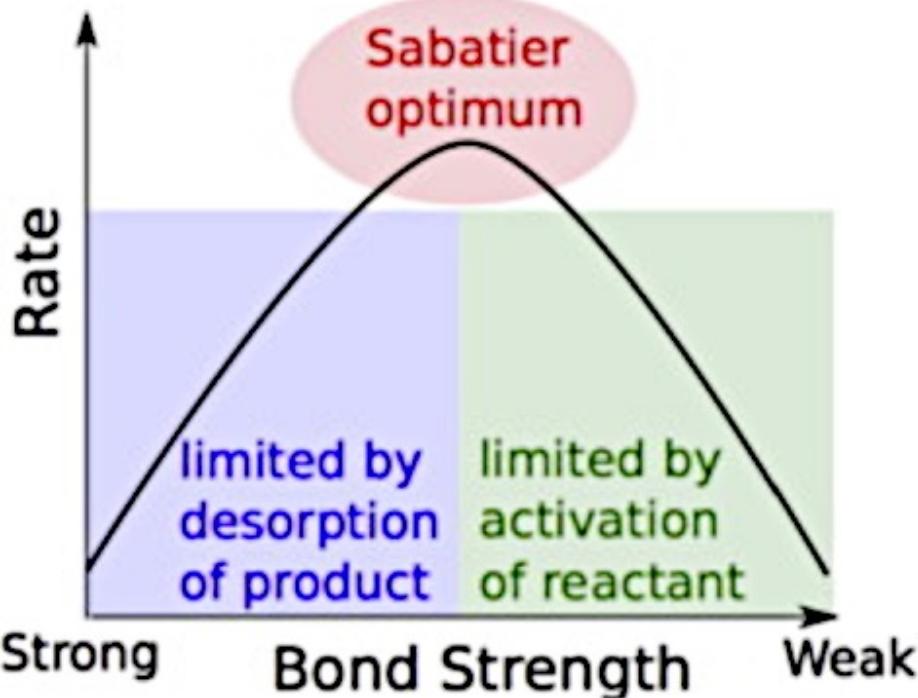




$$k = k_0 e^{-E^*/RT}$$

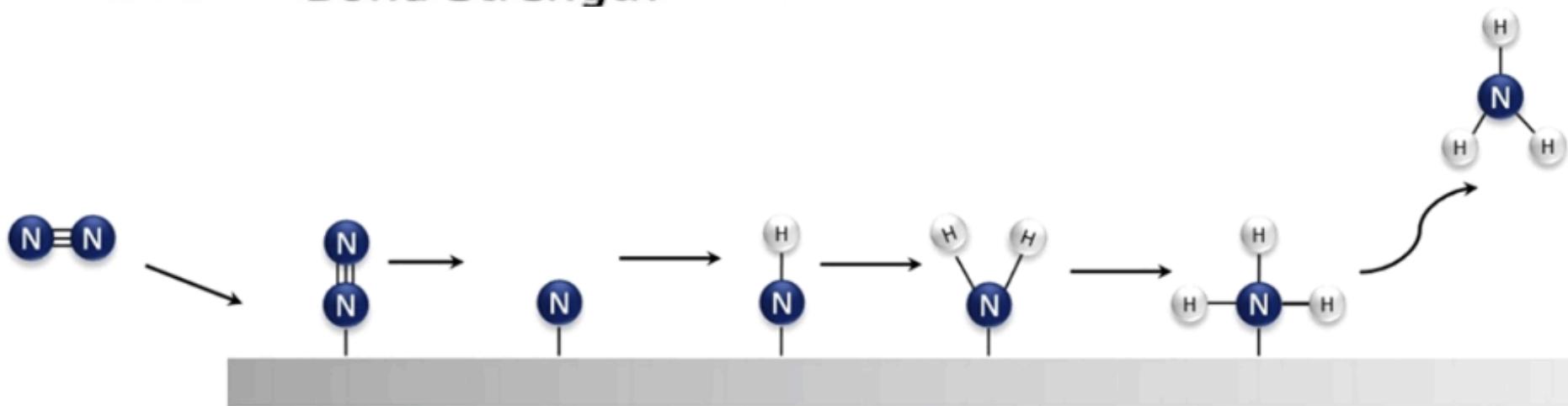
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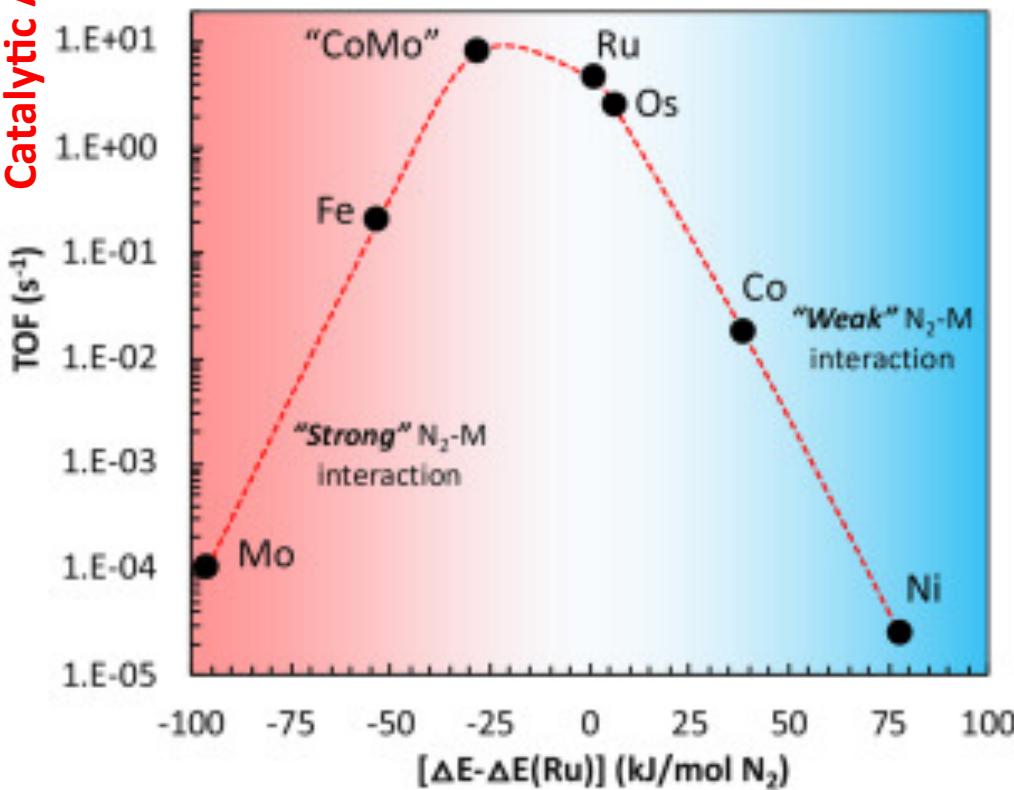
$$k = k_0 e^{-E^*/RT}$$

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Catalytic Activity

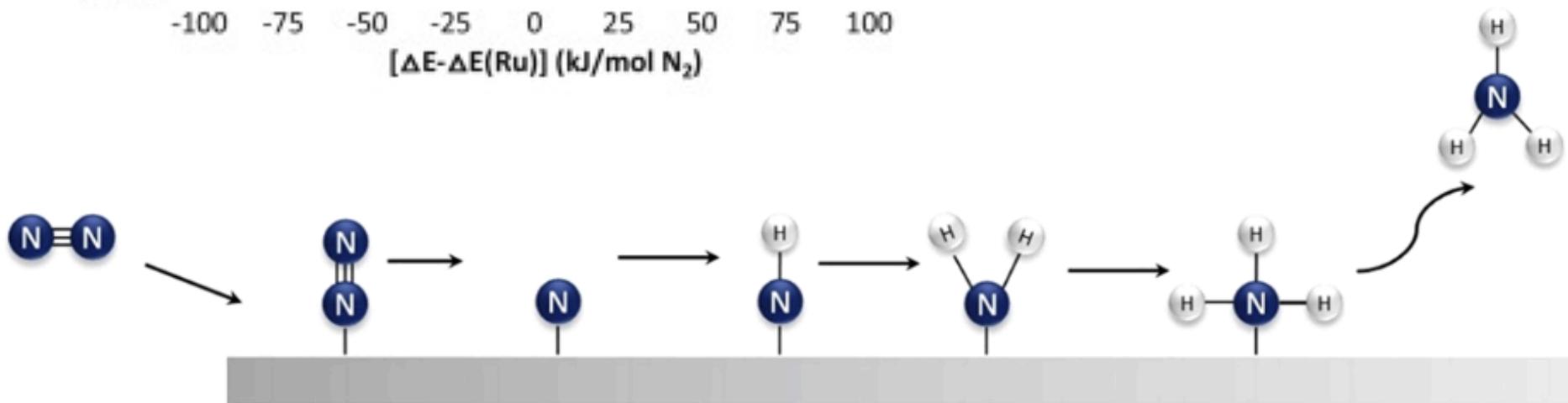
TOF: is defined as the number of the molecules produced per catalytic site.



$$\text{TON} = \frac{\text{Number of product molecules}}{\text{Number of active sites}}$$

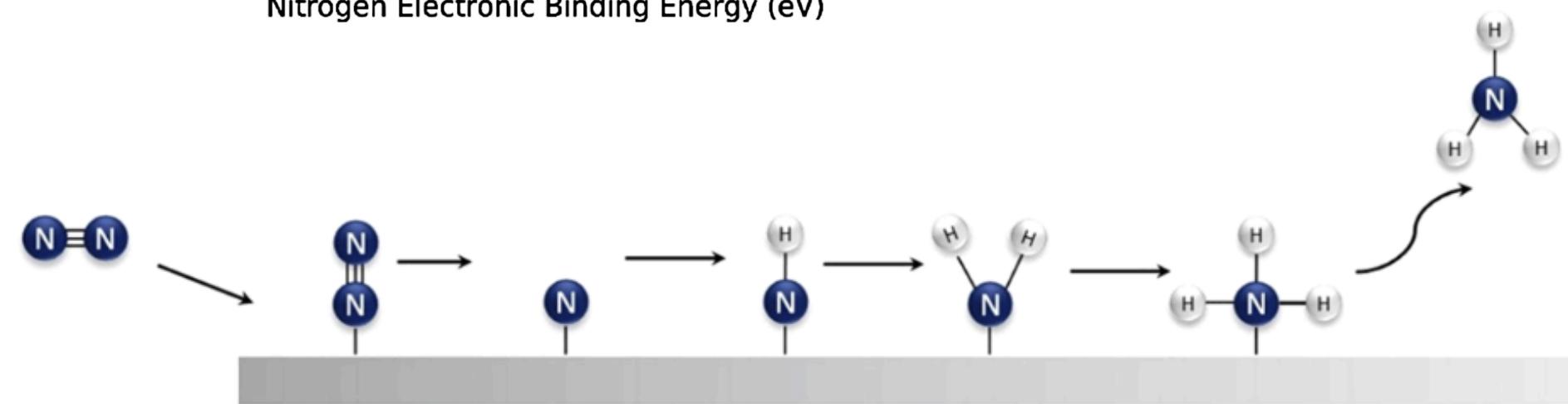
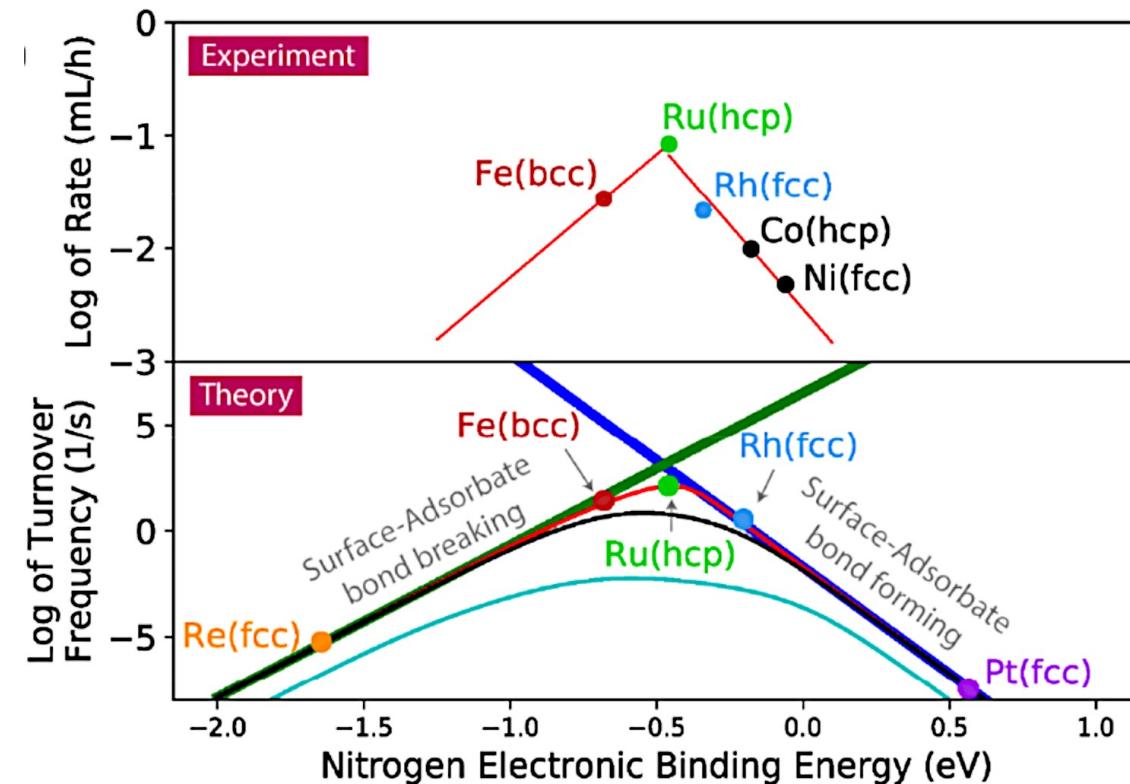
$$k = k_0 e^{-E^*/RT}$$

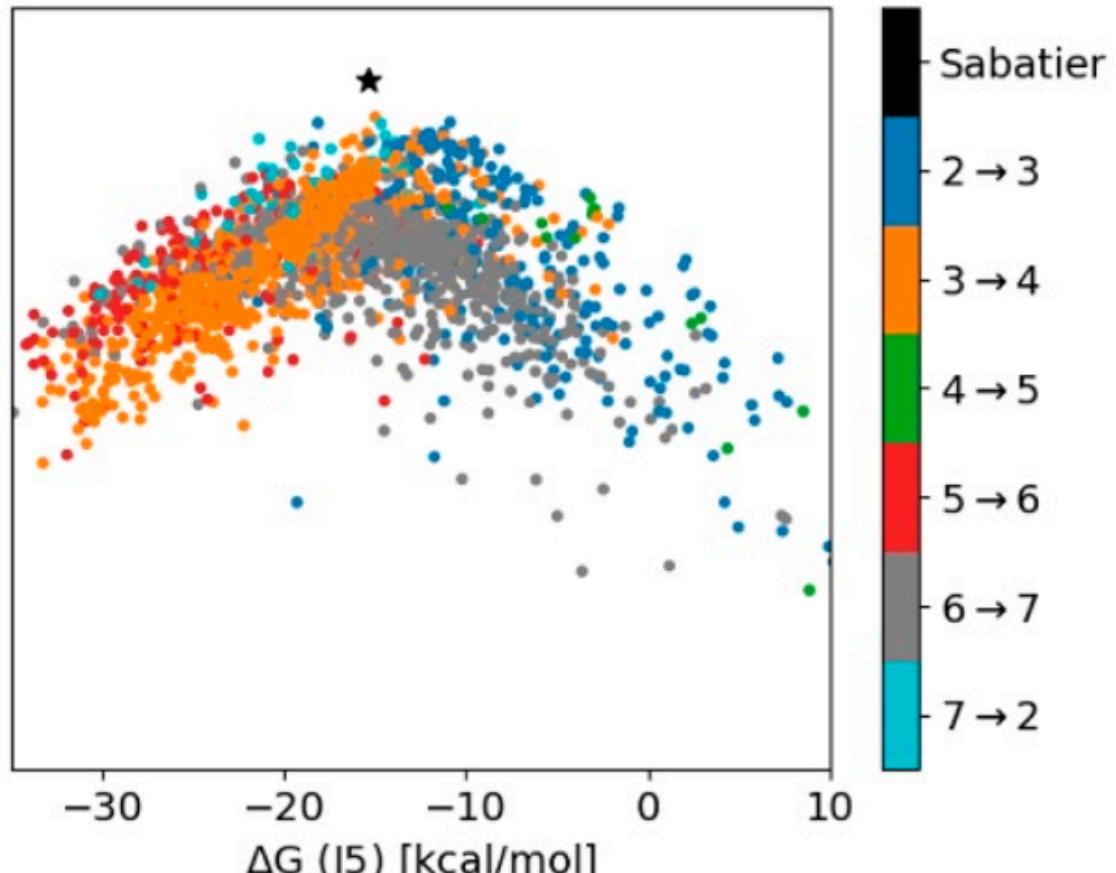
Interactions between the catalyst and the substrate should be "just right" – The Sabatier principle.



$$k = k_0 e^{-E^*/RT}$$

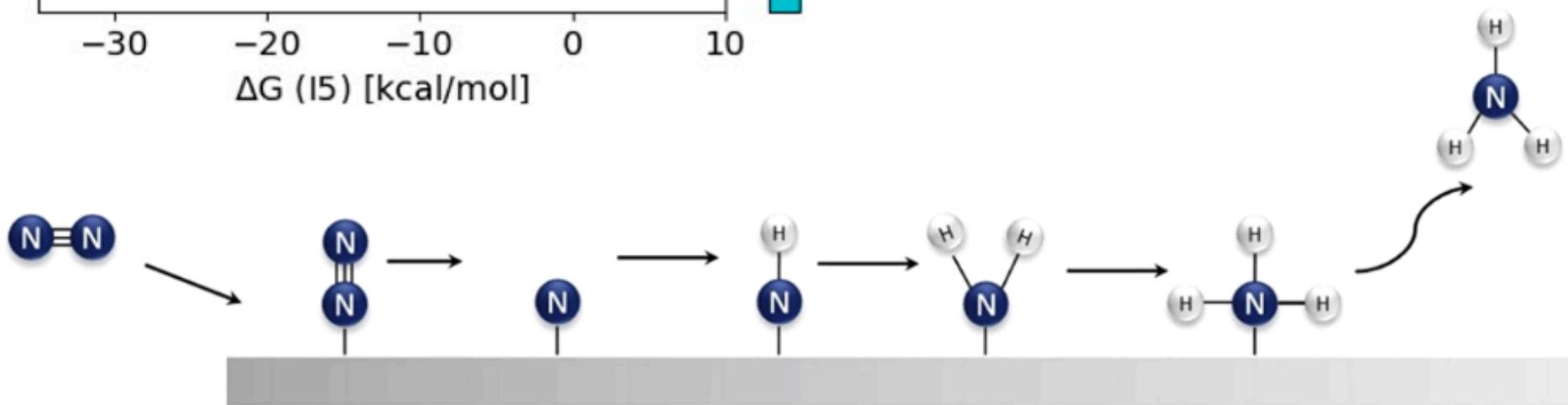
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$$k = k_0 e^{-E^*/RT}$$

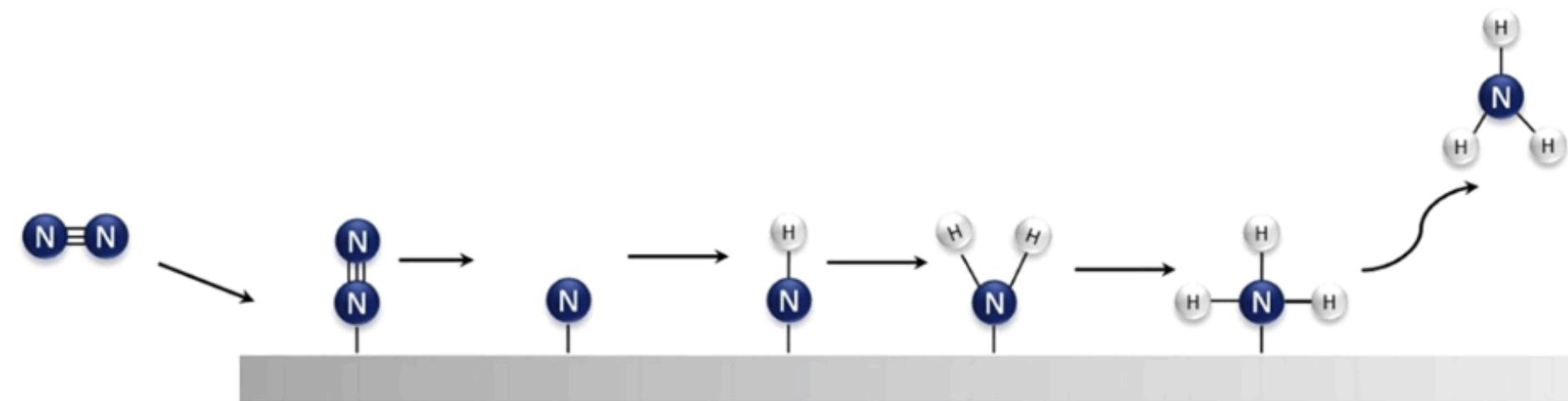
Interactions between the catalyst and the substrate should be "just right" – The Sabatier principle.



Scaling relations allow the activation energies and hence the kinetics of a full catalytic reaction to be expressed as a function of these few bond energies or descriptors in what is known as volcano plots, which provide rationalization of experimental results and serve as a tool for suggesting new catalysts.

$$k = k_0 e^{-E^*/RT}$$

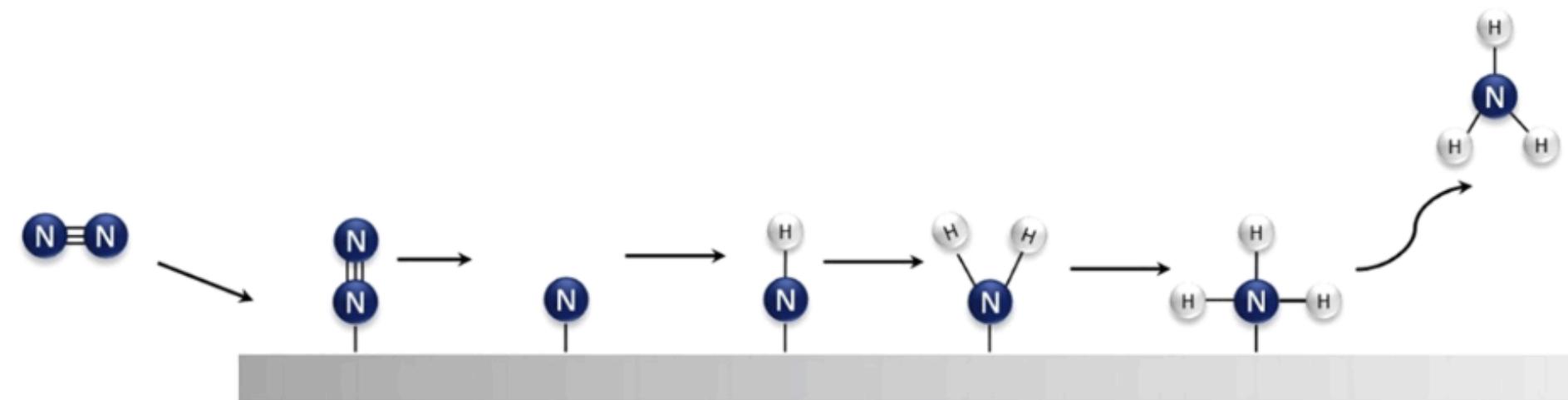
Interactions between the catalyst and the substrate should be "just right" – The Sabatier principle.



Sabatier principle is based on pure thermodynamic considerations, whereas experiments always contain the influence of kinetics. Therefore, there is a conceptual gap between the Sabatier principle and the activity in real experiments.

$$k = k_0 e^{-E^*/RT}$$

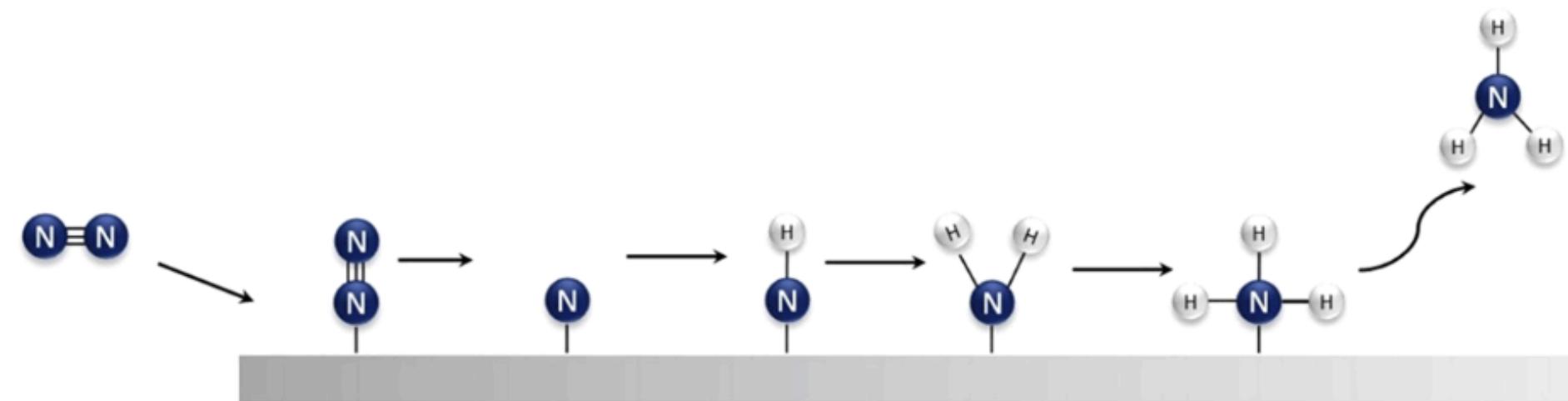
Interactions between the catalyst and the substrate should be "just right" – The Sabatier principle.



Brønsted (Bell) – Evans – Polanyi (BEP) relationship, which states that the free-activation energy (ΔE^*) is linearly correlated with the reaction free energy (ΔG).

$$k = k_0 e^{-E^*/RT}$$

Interactions between the catalyst and the substrate should be "just right" – The Sabatier principle.



For a dissociation reaction:

$\text{AB} \rightarrow \text{A} + \text{B}$, the transition state energy (E_{ts}) is calculated by

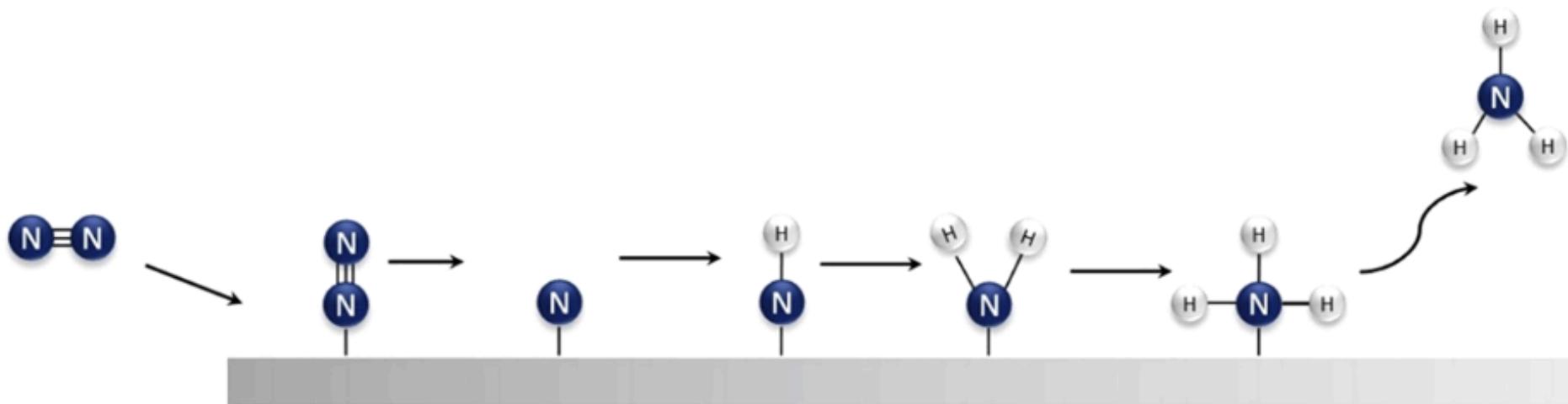
$$E_{ts} = E_{ts/slab} - E_{slab} - E_{gas} \quad (1)$$

$$\Delta E_{diss} = E_{A/slab} + E_{B/slab} - 2E_{slab} - E_{gas} \quad (2)$$

$$k = k_0 e^{-E^*/RT}$$

(BEP) states that the TS energy (E_{ts}) is linearly correlated with the dissociation (ΔE_{diss}).

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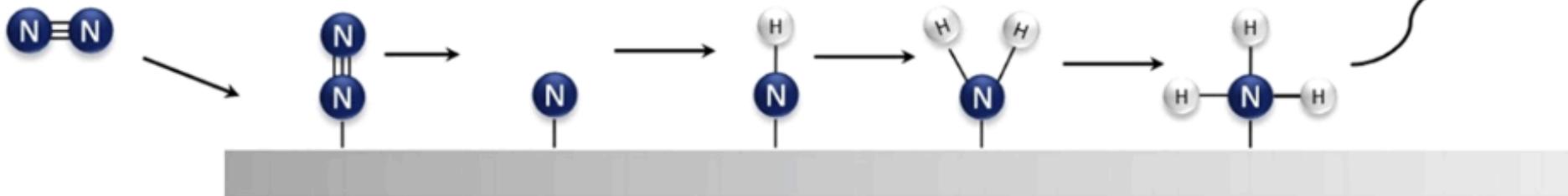
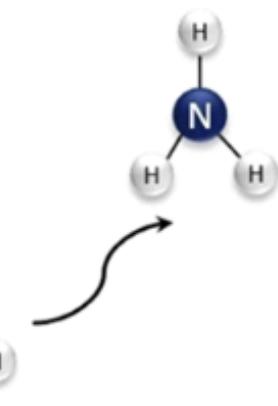
The linear BEP relation, where γ is the slope and ξ is the intercept of the linear relationship between the transition state energies and the reaction energies.

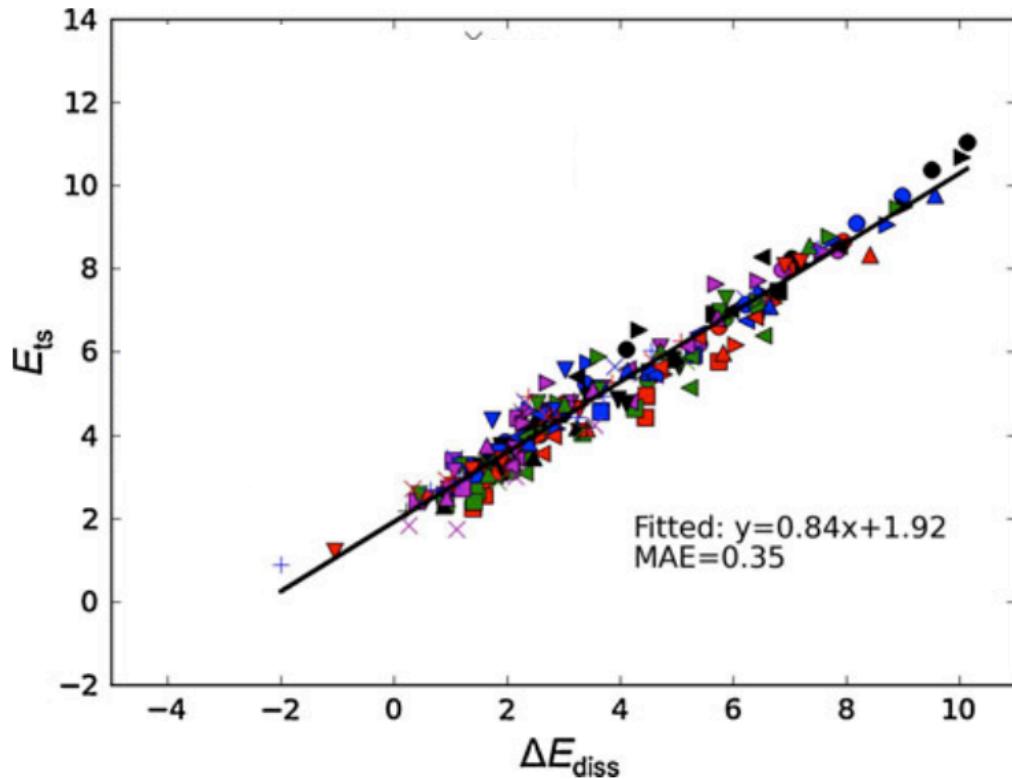
$$E_{ts} = \gamma \Delta E_{diss} + \xi$$

$$k = k_0 e^{-E^*/RT}$$

(BEP) states that the TS energy (E_{ts}) is linearly correlated with the dissociation (ΔE_{diss}).

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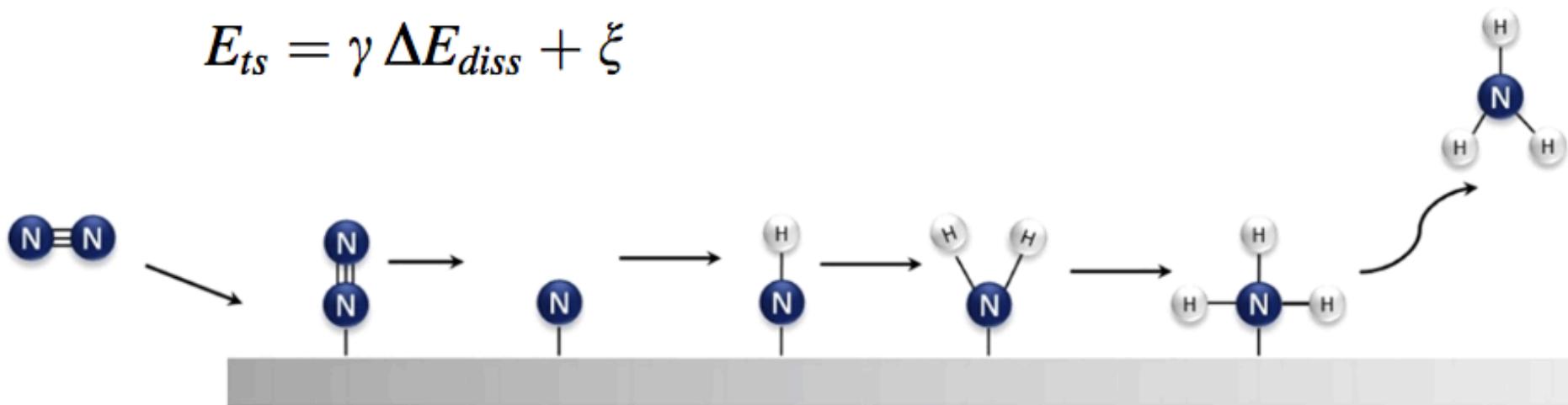


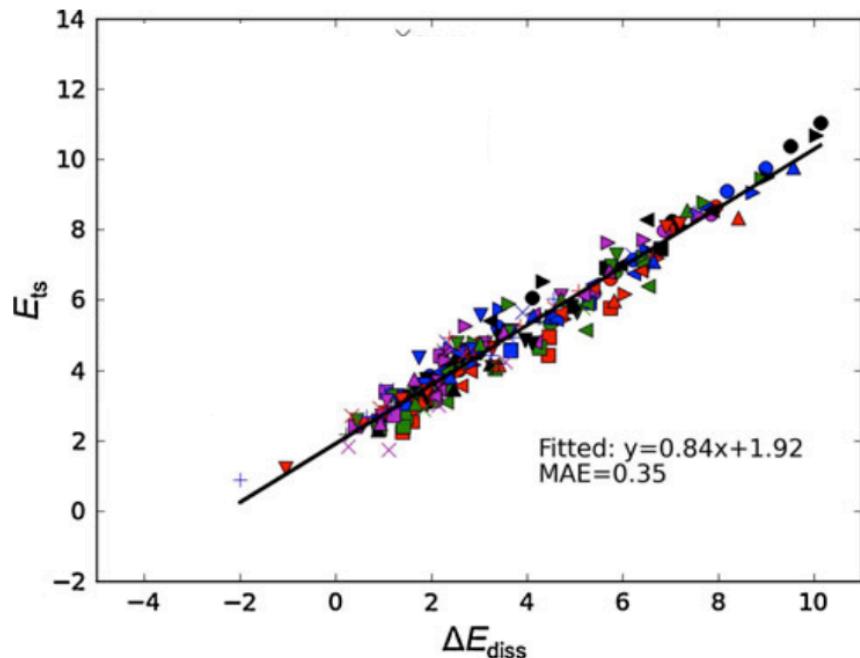
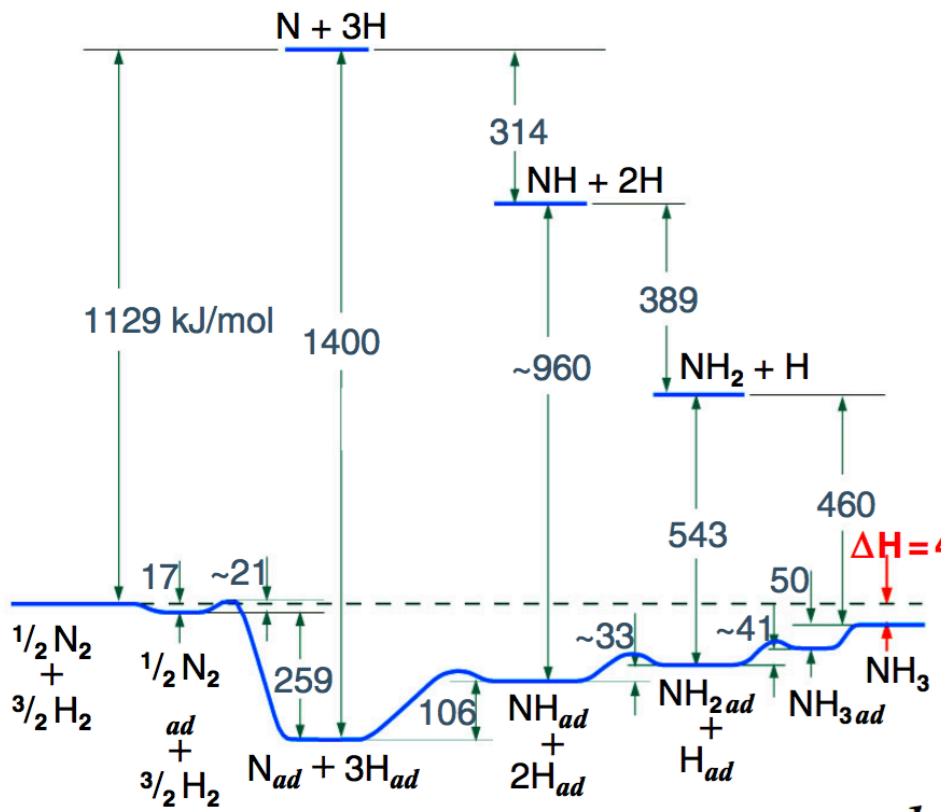


$$k = k_0 e^{-E^*/RT}$$

(BEP) states that the TS energy (E_{ts}) is linearly correlated with the dissociation (ΔE_{diss}).

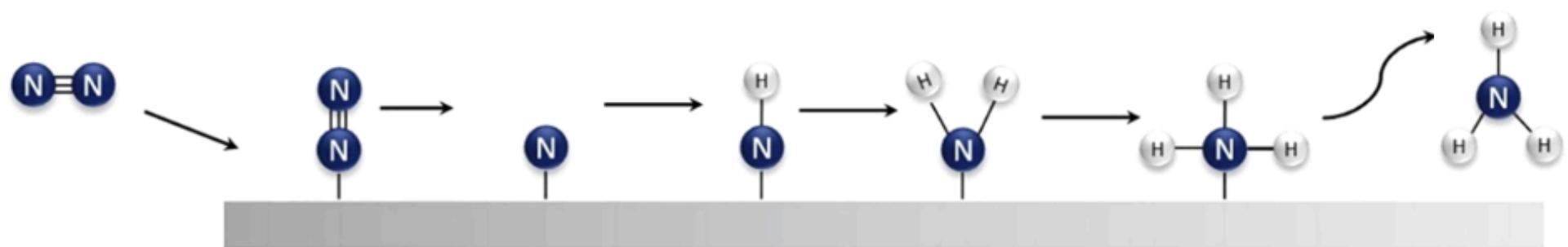
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$$k = k_0 e^{-E^*/RT}$$

$$E_{ts} = \gamma \Delta E_{diss} + \xi$$



TST says that N_2 dissociation is by far the slowest step that is the rate limiting step.

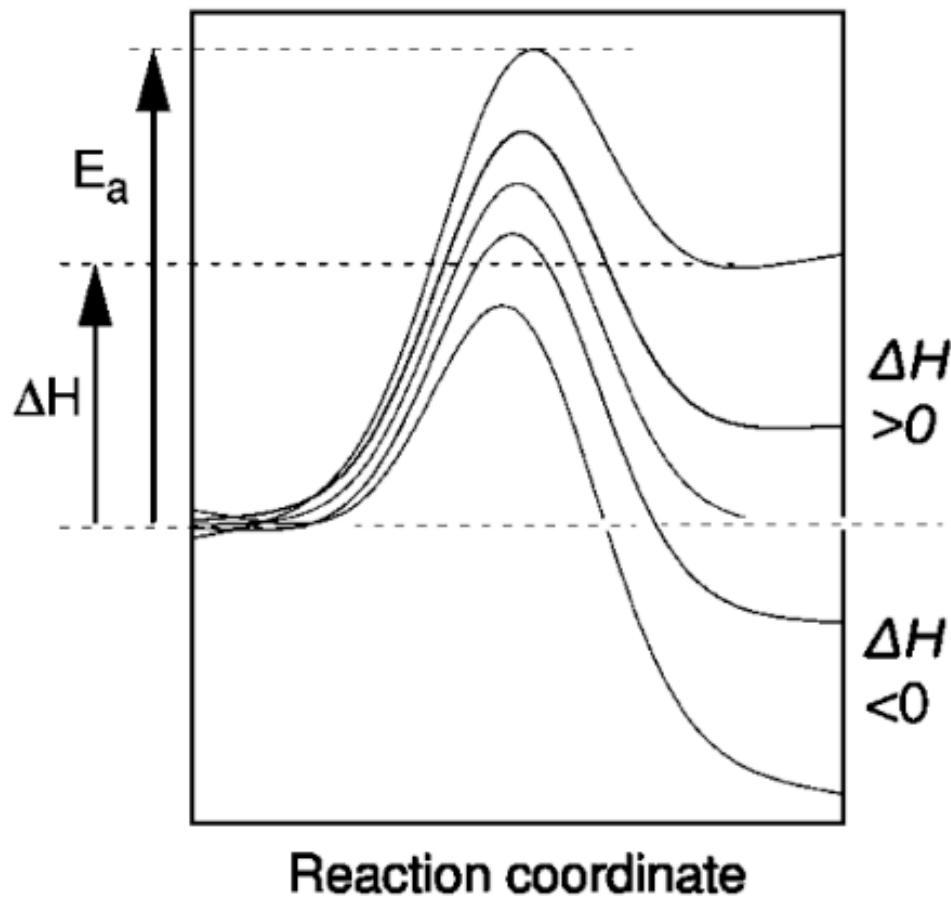
-- The rates of catalytic processes are governed by the adsorption energies of reaction intermediates and activation energies along pathways that connect these intermediates.

- The rates of catalytic processes are governed by the adsorption energies of reaction intermediates and activation energies along pathways that connect these intermediates.
- For a wide range of reactions on a variety of catalyst surfaces, it has been shown that the adsorption energies of various intermediates are correlated to one another by linear scaling relationships.

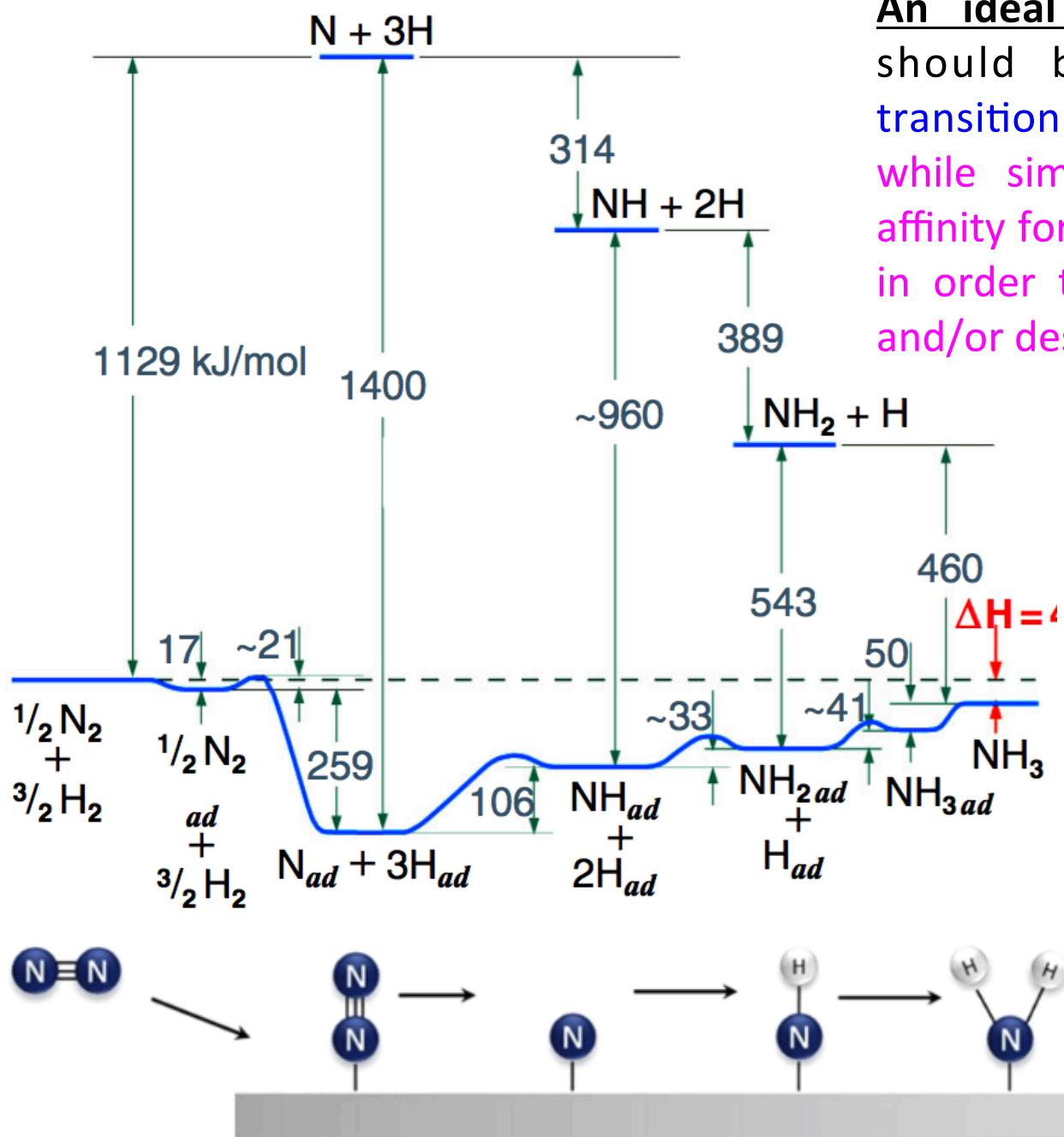
- The rates of catalytic processes are governed by the adsorption energies of reaction intermediates and activation energies along pathways that connect these intermediates.
- For a wide range of reactions on a variety of catalyst surfaces, it has been shown that the adsorption energies of various intermediates are correlated to one another by linear scaling relationships.
- The activation energies are typically linearly related to adsorption energies through Brønsted (Bell)–Evans–Polanyi relationships.

$$E_a = \alpha(\Delta H)$$

Where E_a is the activation energy and ΔH is the reaction enthalpy with respect to the reference system. The proportionality constant (α) characterizes the location of the transition states along the reaction coordinate.



See the Assignment
Problem Tomorrow



An ideal catalyst for this reaction should be able to stabilize the transition state for N_2 dissociation while simultaneously having a weak affinity for NH_x ($x=0$ to 2) intermediates in order to not limit further reaction and/or desorption of NH_3 .

The best identified materials, practical rates are only attainable at elevated temperatures (700 K) and pressures (100atm).



Scaling Limits in predicting even
more profitable catalyst!



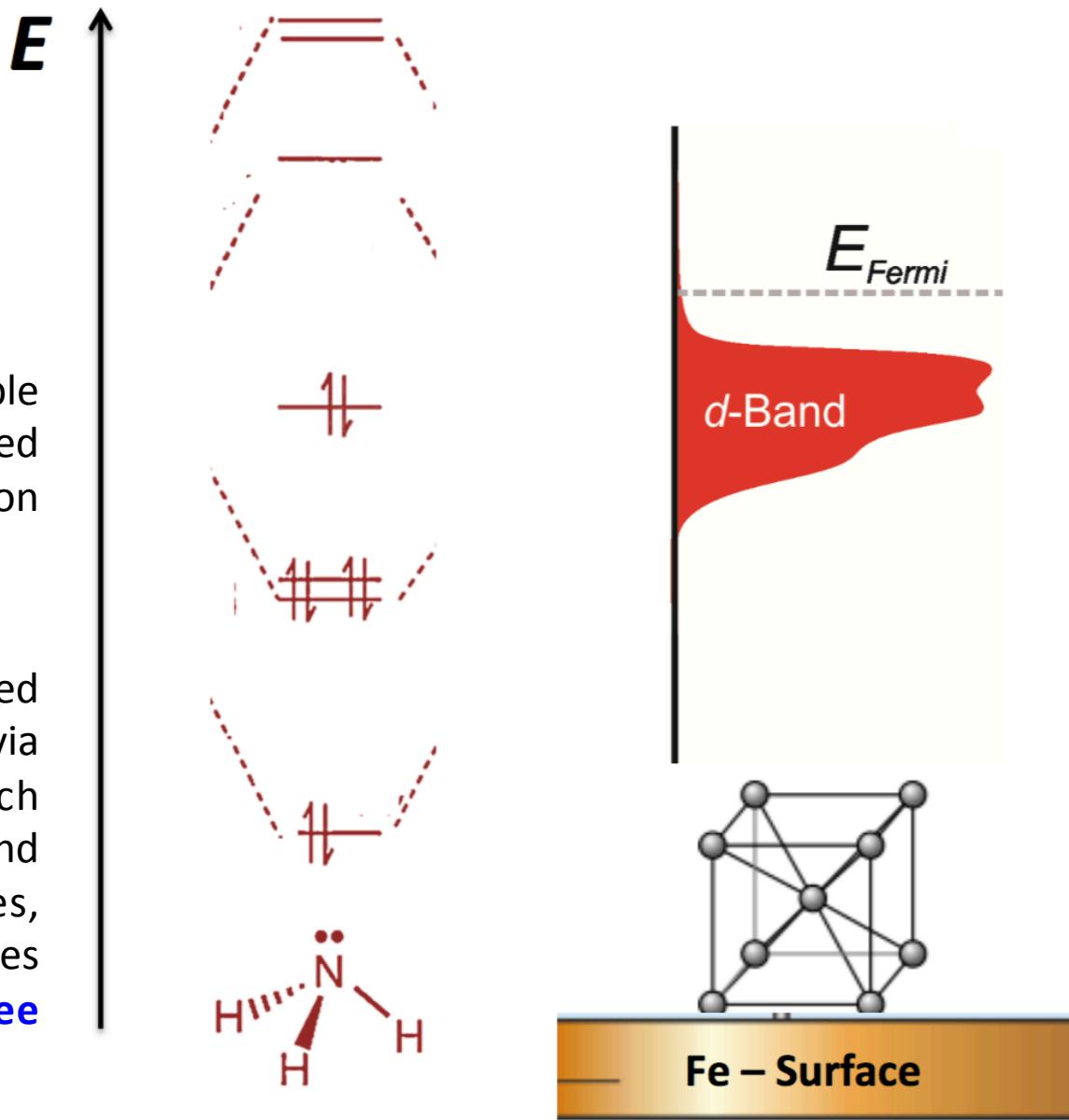
Any Alternatives Suggestions?

Alternatives

-- Assist nitrogen dissociation by applying an external stimulus

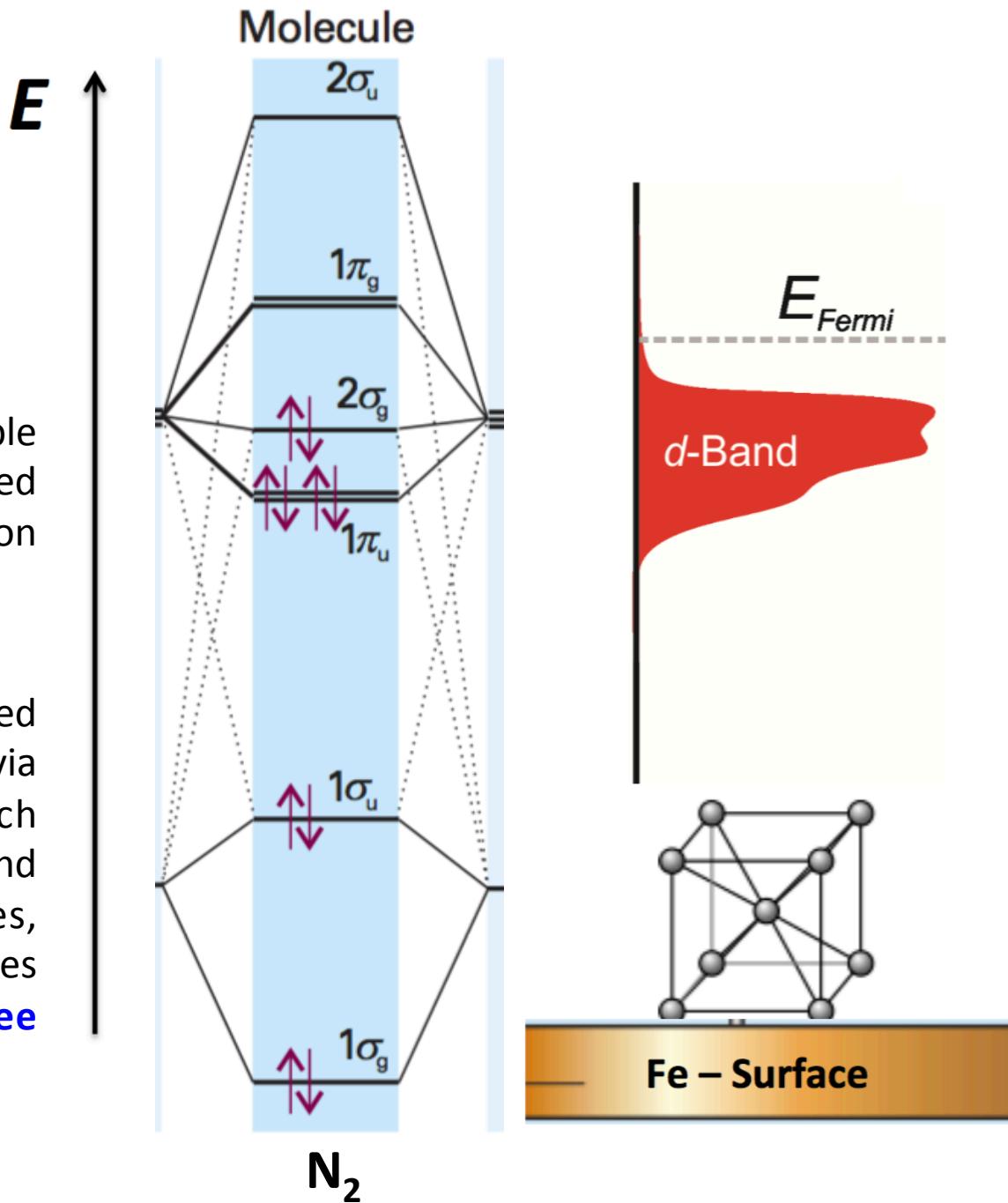
Alternatives

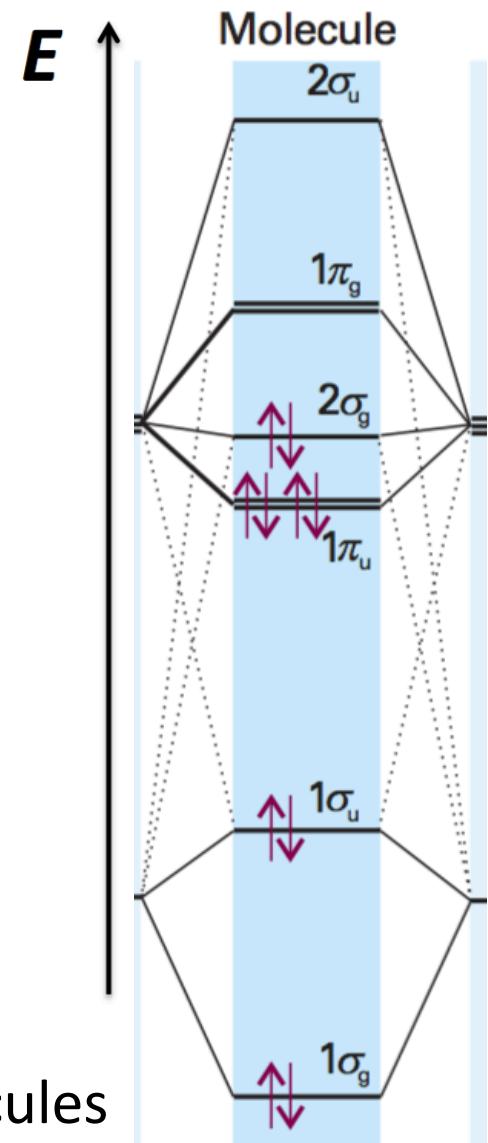
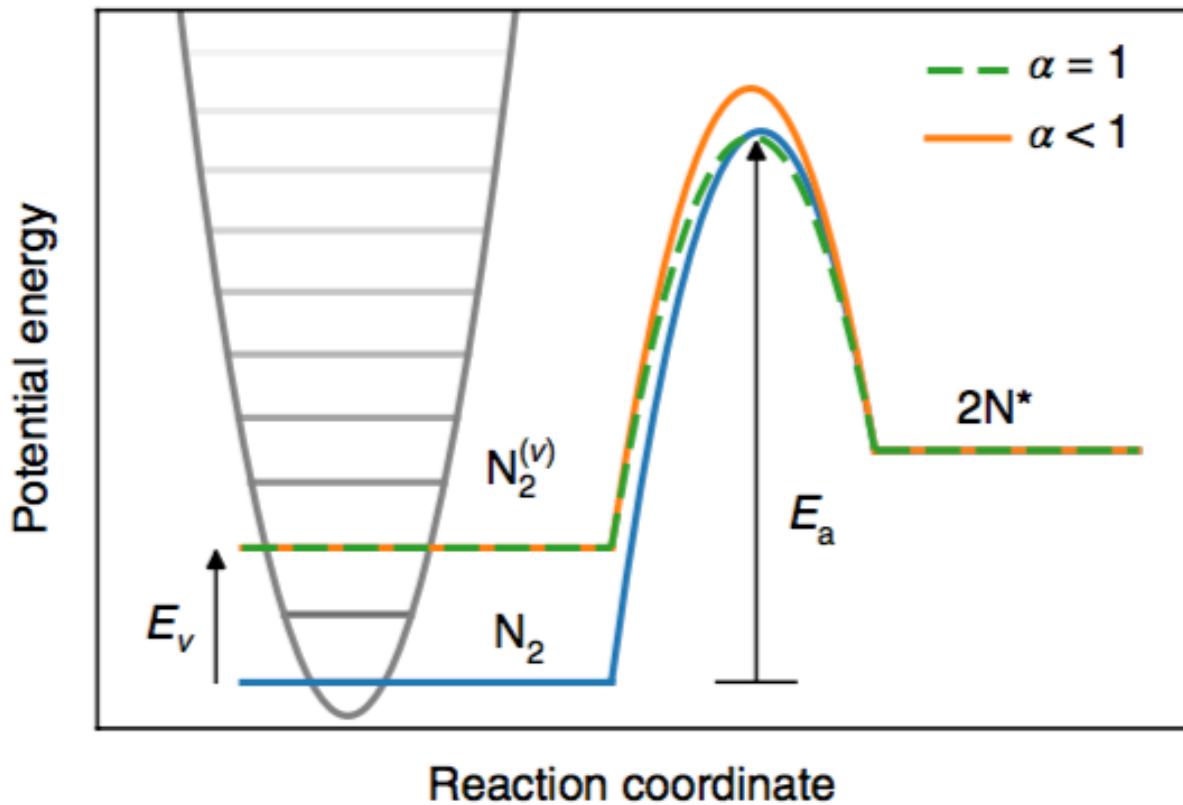
- Assist nitrogen dissociation by applying an external stimulus
- promotion of N₂ into less stable vibrationally or electronically excited states may reduce the activation energy for N₂ dissociation
- Non- thermal plasmas, generated by weakly ionizing the source gas via an electric discharge, are rich sources of such vibrationally and electronically excited molecules, along with other reactive species such as radials, ions and **free electrons.**



Alternatives

- Assist nitrogen dissociation by applying an external stimulus
- promotion of N₂ into less stable vibrationally or electronically excited states may reduce the activation energy for N₂ dissociation
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Vibrationally and electronically excited molecules

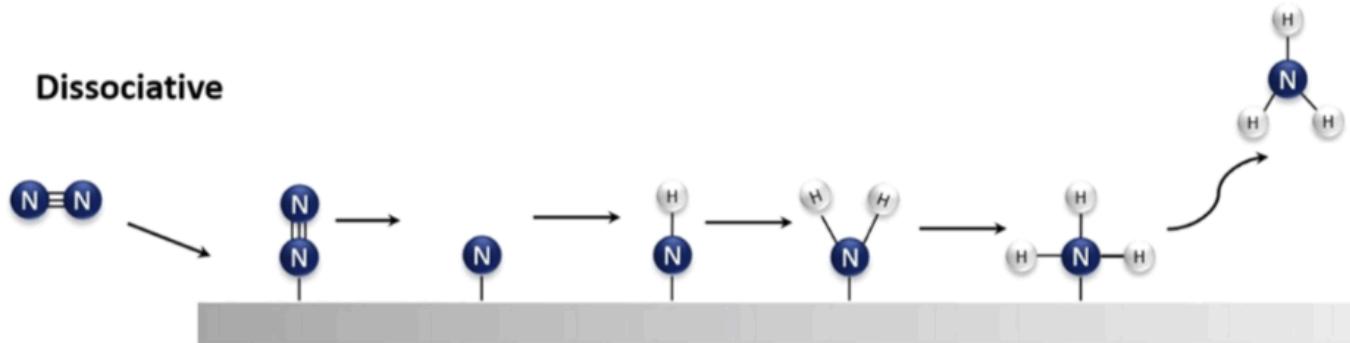
What Are Polanyi's Rules?

Simply stated, Polanyi's rules concern how the barrier location influences the energy requirement and the energy disposal in a direct atom + diatom chemical reaction (11, 12). For an exothermic A + BC reaction, the reaction barrier is usually located in the entrance valley of the reaction, that is, an early barrier. According to Polanyi's rules, reactant translational energy is then more effective than vibration to surmount the barrier to reaction, thus, accelerating the reaction rate. The converse will be true for an endothermic, late-barrier reaction. By the prin-

The rule elucidates the role of different forms of energy (vibration versus translation) in an elementary chemical reaction.

a)

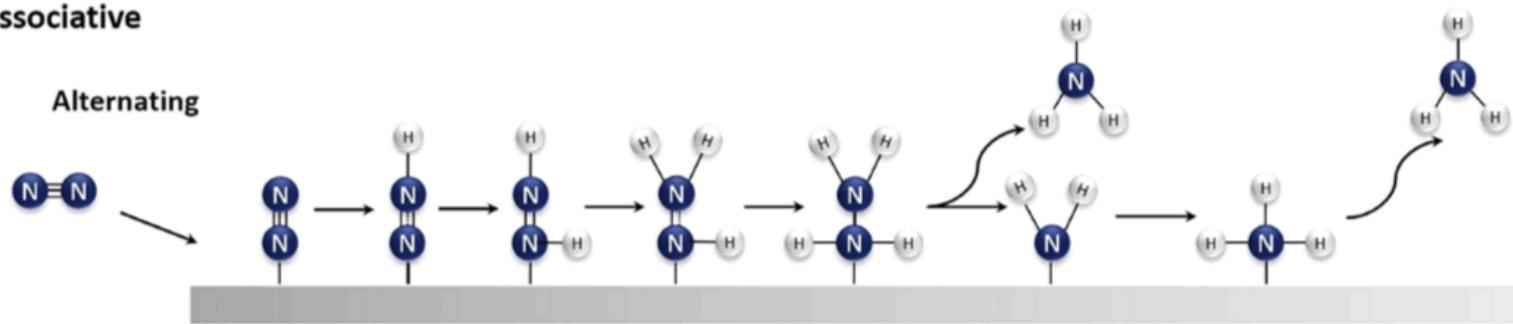
Dissociative



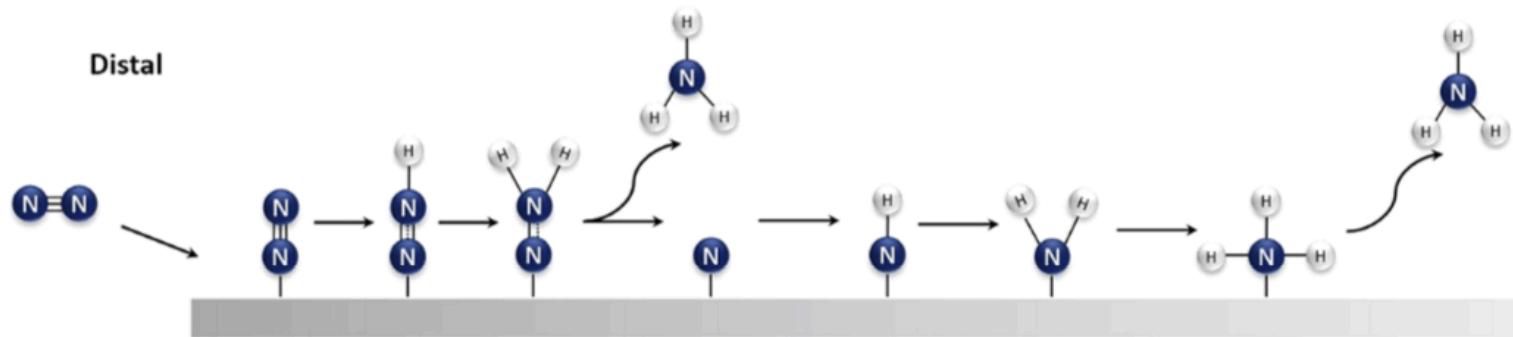
b)

Associative

Alternating

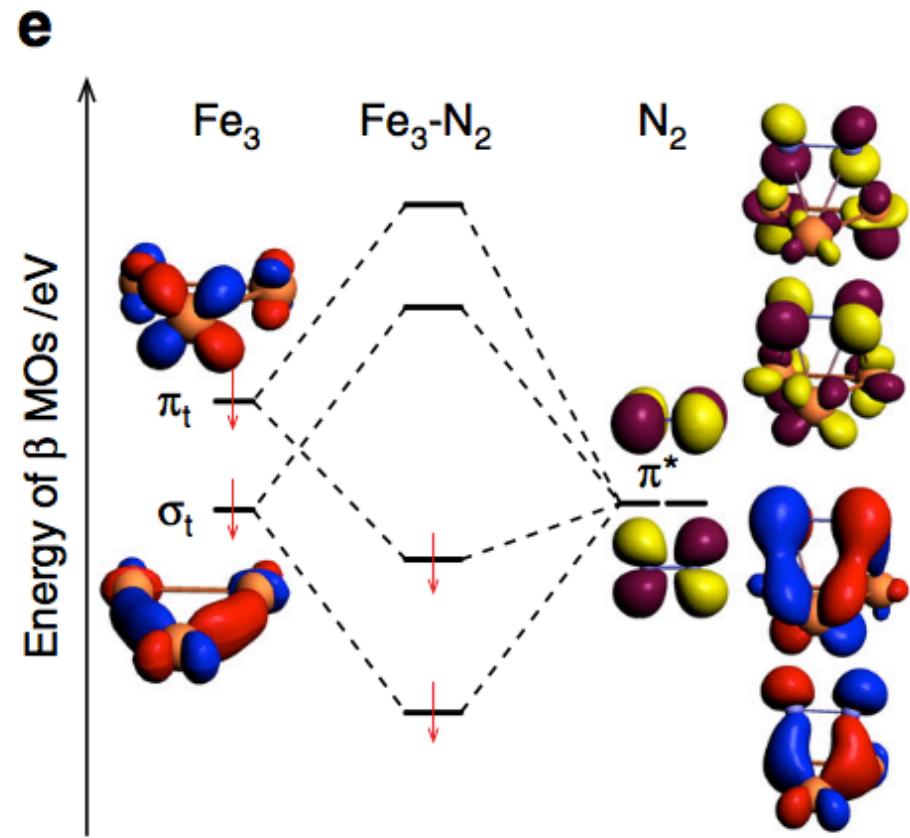
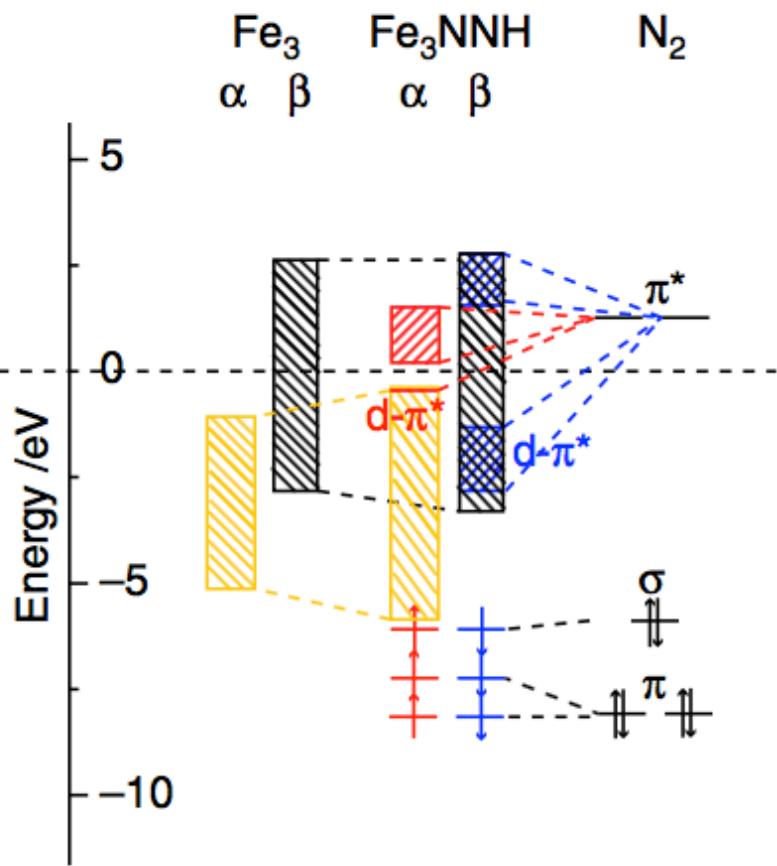


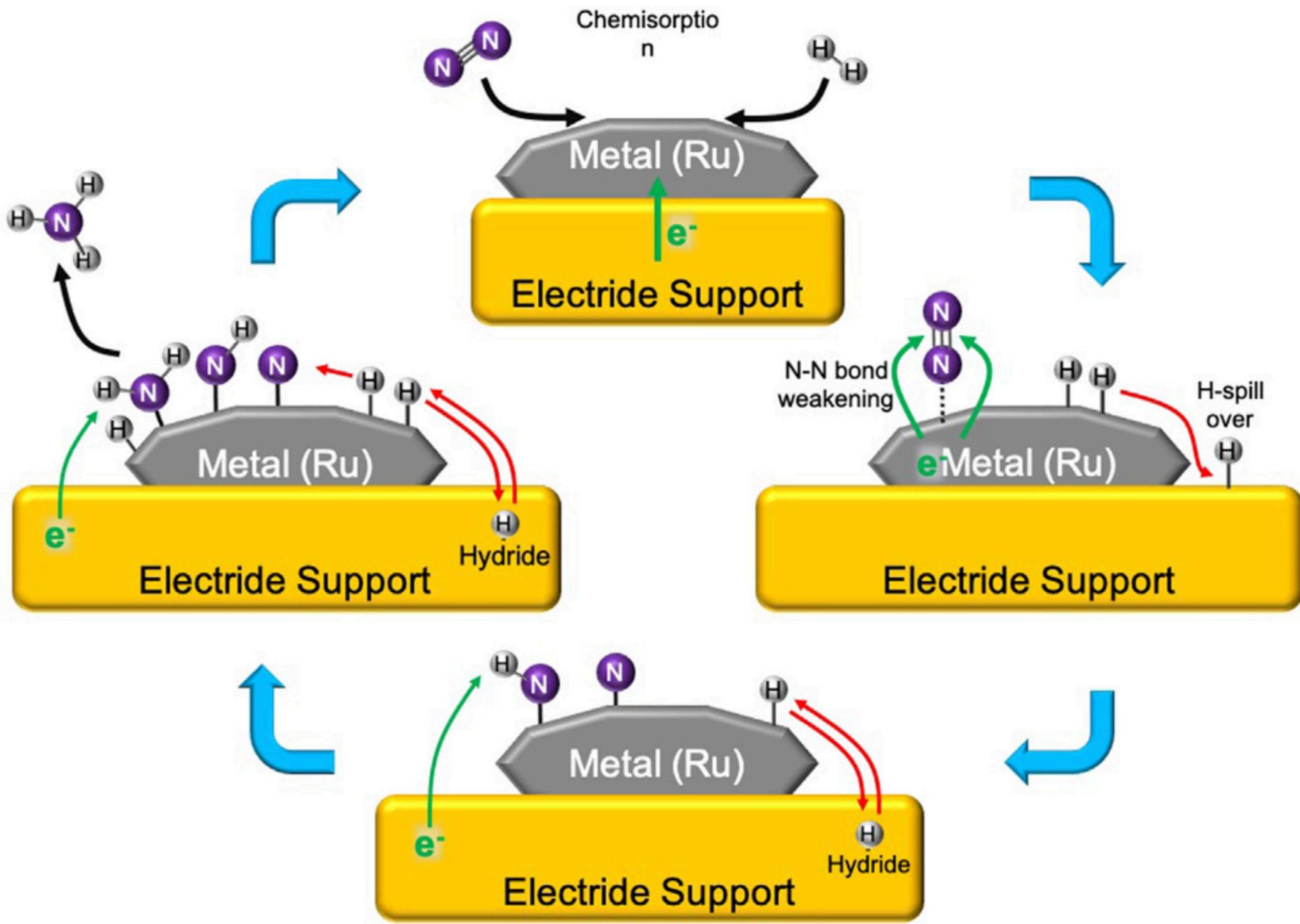
Distal

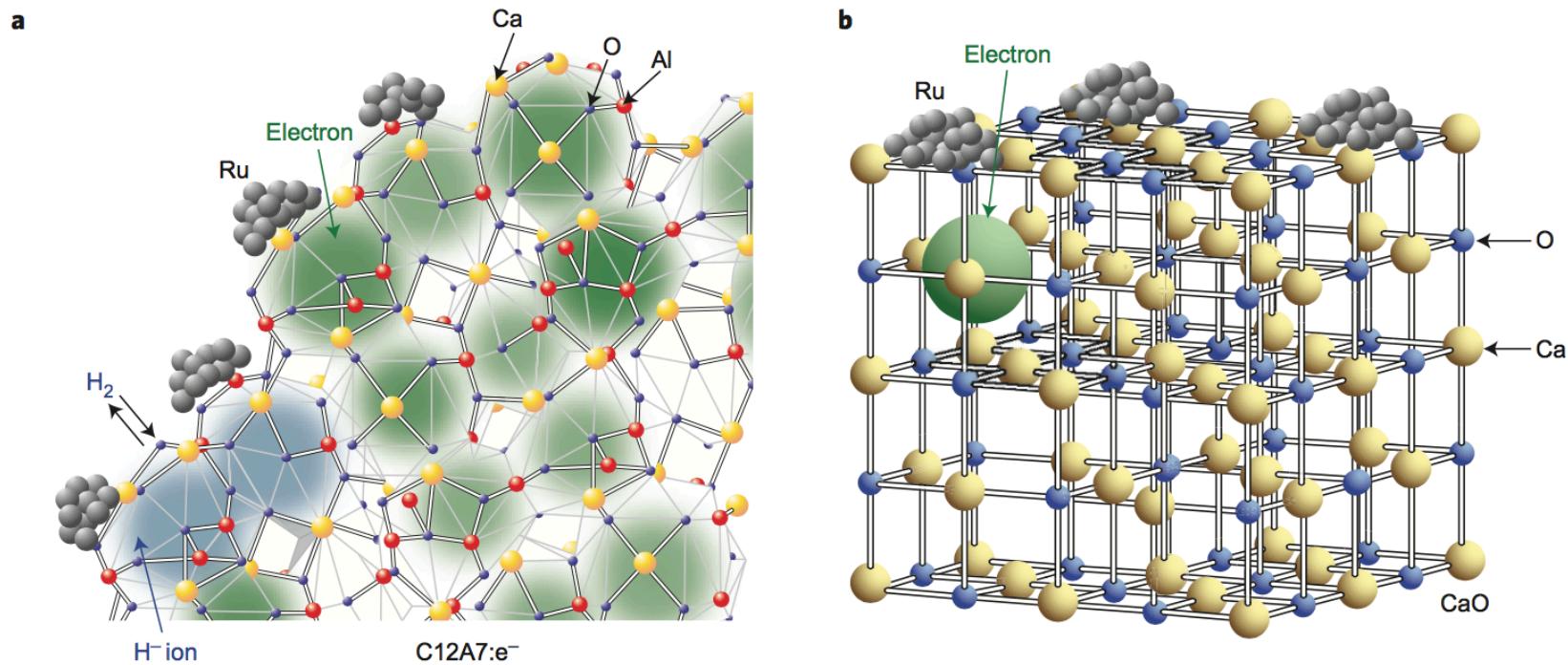


Towards the computational design of solid catalysts

J. K. Nørskov^{1*}, T. Bligaard¹, J. Rossmeisl¹ and C. H. Christensen²







Structural Diversity and Electron Confinement in Li_4N : Potential for 0-D, 2-D, and 3-D Electrides

Yuta Tsuji,[†] Prasad L. V. K. Dasari,^{*,‡} S. F. Elatresh,[§] Roald Hoffmann,^{*,§} and N. W. Ashcroft^{||}

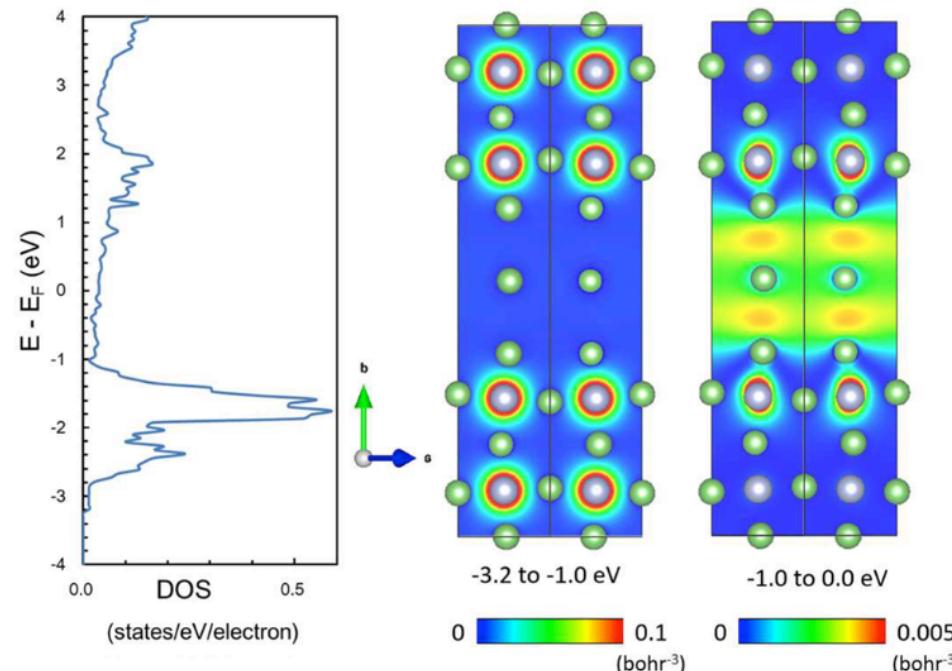
[†]Education Center for Global Leaders in Molecular Systems for Devices, Kyushu University, Nishi-ku, Fukuoka 819-0395, Japan

[‡]Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

[§]Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853, United States

^{||}Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, United States

 Supporting Information



QM-Mechanism-Based Hierarchical High-Throughput *In Silico* Screening Catalyst Design for Ammonia Synthesis

Qi An,^{*,†,‡,§,ID} Yidi Shen,[‡] Alessandro Fortunelli,^{*,†,§,ID} and William A. Goddard, III^{*,†,ID}

[†]Materials and Process Simulation Center (MSC), California Institute of Technology, Pasadena, California 91125, United States

[‡]Department of Chemical and Materials Engineering, University of Nevada—Reno, Reno, Nevada 89577, United States

[§]CNR-ICCOM, ThC2-Lab, Consiglio Nazionale delle Ricerche, Pisa 56124, Italy

 Supporting Information

$$k_{\text{TST}} = \frac{k_{\text{B}} T}{b} (c^{\circ})^{\Delta v^{\ddagger}} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right)$$

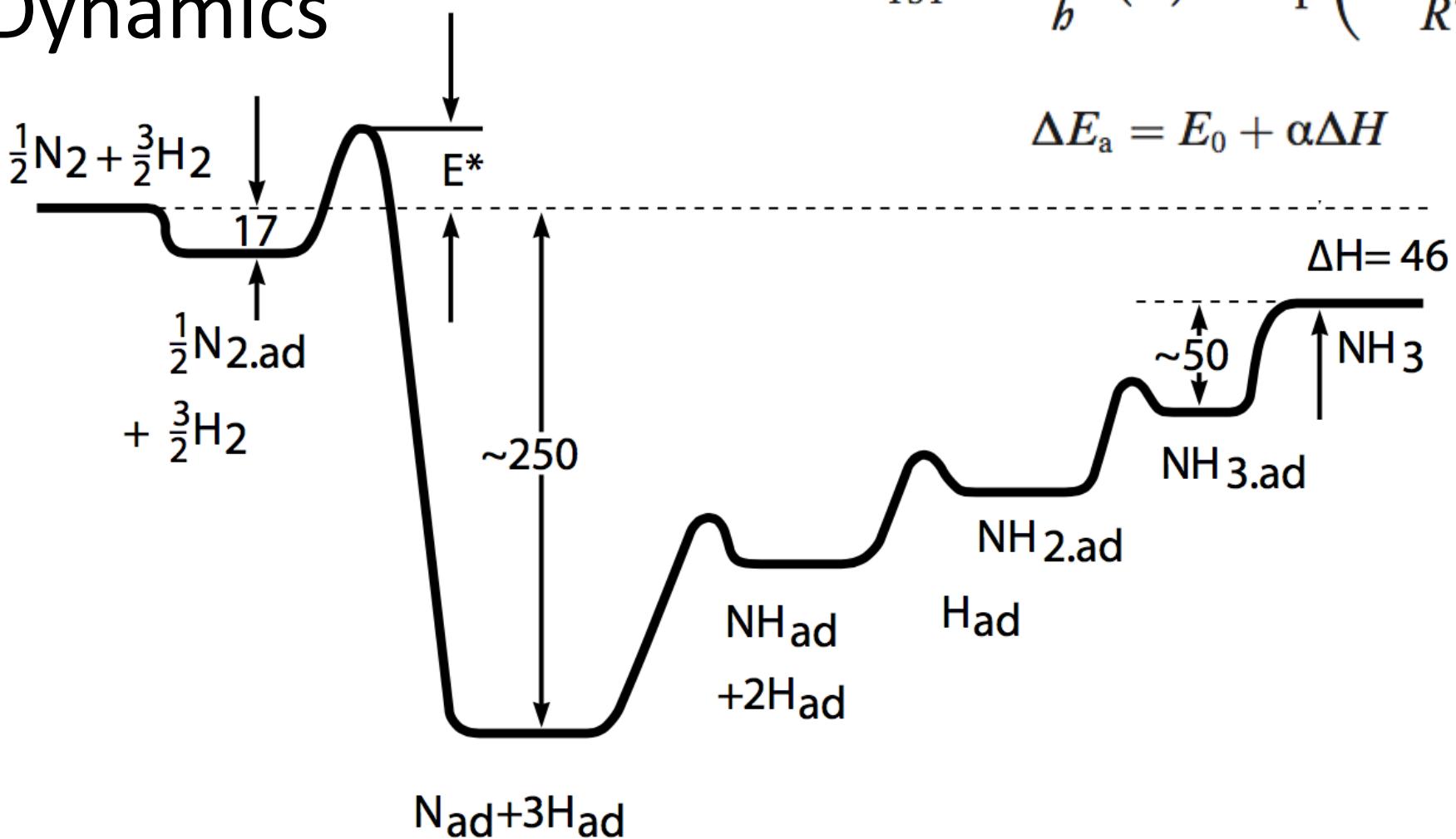
ABSTRACT: We propose and test a hierarchical high-throughput *in silico* screening approach to catalyst design for complex catalytic reaction systems.

change in the free-energy barrier. In other words, we explicitly calculated only the free-energy of reference states. In general, the free-energy of transition states can be explicitly calculated or estimated via Brønsted–Evans–Polanyi (BEP) relations,^{4,5,19}

effect of the catalyst changes on each barrier. This allows us to test new candidates with only 1% of the effort for a full calculation. Thus, we were able to quickly screen 34 candidate dopants to select a small subset (Rh, Pt, Pd, Cu) that satisfy all criteria, including stability. Then from these four candidates expected to increase the TOF for NH₃ production, we selected the best candidate (Rh) for a more complete free-energy and kinetic analysis (10 times the effort for HHTS but still 10% of the effort for a complete analysis of the full reaction network). We predict that Rh doping of Fe will increase the TOF for NH₃ synthesis by a factor of ~3.3 times compared to Fe(111), in excellent agreement with our HHTS predictions, validating this approach.

Chemical Reaction Dynamics

$$k_{\text{TST}} = \frac{k_{\text{B}} T}{b} (c^{\circ})^{\Delta v^{\dagger}} \exp\left(-\frac{\Delta G^{\circ\dagger}}{RT}\right)$$



An energy diagram showing the progression of the reaction from the reactants N_2 and H_2 to the product NH_3 . Energies are given in units of kJ/mol. (Adapted from Ertl 1983)

The best identified materials, practical rates are only attainable at elevated temperatures (700 K) and pressures (100atm).

Alternatives Suggestions?



