Reaction Kinetics

by

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Chemical Kinetics

- Study of reaction rates
- Why?
  - feasibility of reaction
  - competition with other reactions
  - to understand how reactions occur on a molecular level

Variables

Rates of chemical reactions are primarily controlled by 5 factors:

- the chemical nature of the reactants
- the ability of the reactants to come in contact with each other
- the concentrations of the reactants
- the temperature of the reacting system
- the availability of catalysts that affect the rate of the reaction but are not themselves consumed.

Catalysts

- substances that increase the rates of chemical reactions without being used up, e.g. enzymes

Rates of chemical reactions

$$\text{Rate of reaction} = \frac{\text{change in concentration}}{\text{change in time}}$$

$$= \frac{\Delta \text{conc}}{\Delta t} \quad \text{mol dm}^{-3}\ \text{s}^{-1}$$

Measuring reaction rates

- average rate
- instantaneous rate
- initial rate

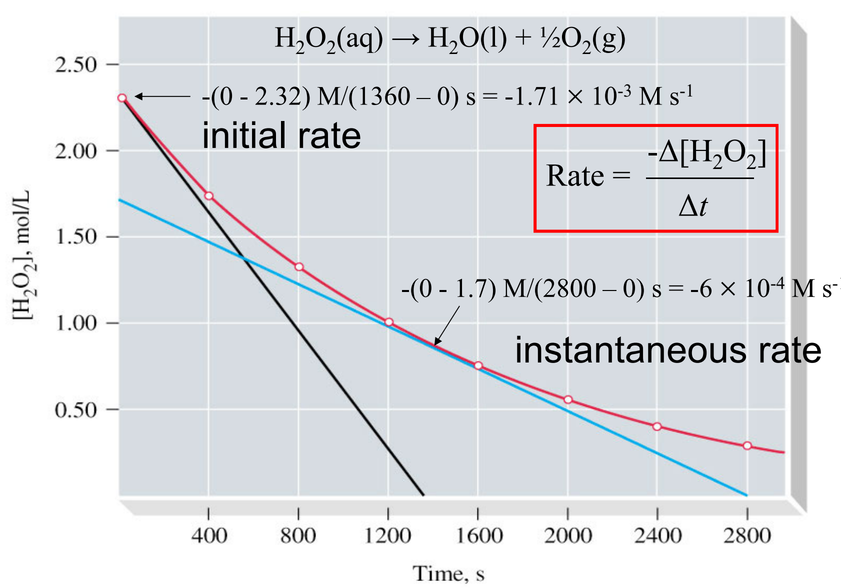
$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

TABLE 15.2 Decomposition of H_2O_2—Derived Rate Data

I Time, s	II Δt, s	III $[H_2O_2]$, M	IV $\Delta[H_2O_2]$, M	V Reaction Rate $-\Delta[H_2O_2]/\Delta t$, $M\ s^{-1}$
0		2.32		
	400		−0.60	15.0×10^{-4}
400		1.72		
	400		−0.42	10.5×10^{-4}
800		1.30		
	400		−0.32	8.0×10^{-4}
1200		0.98		
	400		−0.25	6.3×10^{-4}
1600		0.73		
	400		−0.19	4.8×10^{-4}
2000		0.54		
	400		−0.15	3.8×10^{-4}
2400		0.39		
	400		−0.11	2.8×10^{-4}
2800		0.28		

Average rate over the time interval Δt.

Note that the rate decreases as the reaction proceeds.



Because the amounts of products and reactants are related by stoichiometry, any substance in the reaction can be used to express the reaction rate.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

propane oxygen carbon dioxide water

- O_2 is reacting 5x faster than propane.
- CO_2 is formed 3x faster than propane is reacting.
- H_2O is formed 4x faster than propane is reacting.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

- concentration of reactants decrease –ve
- concentration of products increase +ve

$$\text{Rate} = -\frac{d[C_3H_8]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = \frac{1}{3}\frac{d[CO_2]}{dt} = \frac{1}{4}\frac{d[H_2O]}{dt}$$

rate of decrease of concentration with time

rate of increase of concentration with time

Example

In the reaction 2A + B $\rightarrow$ C + 3D, reactant A is found to disappear at the rate of 6.2 x 10^{-4} mol dm^{-3} s^{-1}.

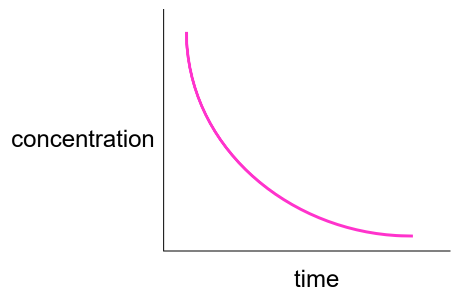
(a) What is the rate of reaction at this point?

(b) What is the rate of disappearance of B?

(c) What is the rate of formation of D?

Change of reaction rate with time

The rate of a reaction changes as the reactants are consumed because the rate depends on the concentrations of reactants.



How does the concentration of a product vary with time?

The steeper the curve, the faster the rate.

Concentration and rate

Rates of reaction change when the concentrations of reactants change. The rate law allows us to calculate the rate of the reaction if the concentrations are known.

Dependence of rate on concentration

$$A + B \rightarrow \text{products}$$

$$\text{Rate} \ \alpha \ [A]^m[B]^n$$

The exponents n and m are determined by experiment. They are often unrelated to the stoichiometric coefficients hence the need to do experiments.

The rate law is given by:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^m[B]^n$$

- k $\equiv$ rate constant
- (m + n) = total order
- m = order with respect to A
- n = order with respect to B

Order can be +ve, –ve or fractional depending on the mechanism.

Rate Law

- The rate law, which tells us how A, B and products disappear or appear with time when their concentrations vary, can only be obtained by experiment – unless it is known that the reaction is elementary.
- elementary reaction – occurs in a single step exactly as written
- To find the exponents in a rate law we study how changes in concentration affect the rate of reaction.

Determining the rate law

$$A + B \rightarrow \text{products}$$

$$\text{rate} = k[A]^m[B]^n$$

initial conc/mol dm^{-3}		initial rate/mol dm^{-3} s^{-1}
[A]	[B]	
0.10	0.10	0.20
0.20	0.10	0.40
0.30	0.10	0.60
0.30	0.20	2.40
0.30	0.30	5.40

rate = $k[A]^m[B]^n$

- [A] doubles, rate doubles
- [A] triples, rate triples
- ⑧ m = 1
- [B] doubles, rate increases by a factor of 4 (2^2)
- [B] triples, rate increases by a factor of 9 (3^2)
- ⑧ n = 2
- rate = $k[A]^1[B]^2$
- $k = \frac{\text{rate}}{[A]^1\,[B]^2} = \frac{0.20}{(0.1)\,(0.1)^2} = 2.0 \times 10^2\ dm^6\ mol^{-2}\ s^{-1}$

Rate Constant

Its value depends on:

- the specific reaction
- the presence of a catalyst (if any)
- the temperature

The larger the value of k, the faster the reaction goes.

The units of k depend on the form of the rate law.

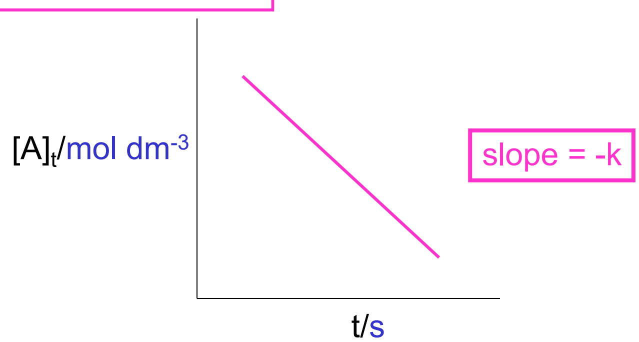
Concentration and time

- We often want to know the concentrations of reactants and products at some specified time after the reaction has started.
- By means of calculus, we can transform a rate law into a mathematical relationship between concentration and time called an integrated rate equation.

Determination of Reaction Order

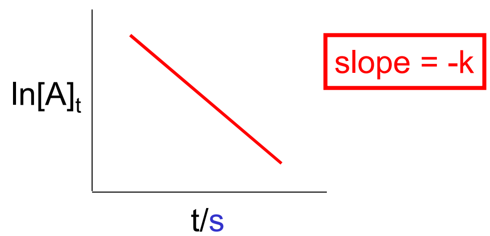
Zero Order

- Rate = $-\frac{d[A]}{dt} = k[A]^0 = k$ mol dm^{-3} s^{-1}
- $[A]_t = -kt + [A]_0$



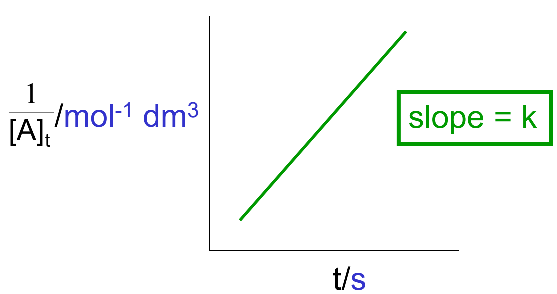
First–order reactions

- Rate = $-\frac{d[A]}{dt} = k[A]^1$
- ⑧ $k = -\frac{1}{[A]}\frac{d[A]}{dt}$ s^{-1}
- $\ln\frac{[A]_o}{[A]_t} = kt$ *or* $\ln[A]_t = -kt + \ln[A]_0$



Second–order reactions

- Rate = $-\frac{d[A]}{dt} = k[A]^2$
- $\therefore\ k = -\frac{1}{[A]^2}\frac{d[A]}{dt}$ $mol^{-1}\ dm^3\ s^{-1}$
- $\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$



Example

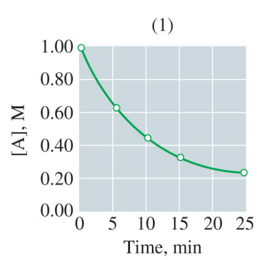
The decomposition of N_2O_5 to NO_2 and O_2 is first order, with a rate constant of 4.80×10^{-4} s^{-1} at 45 °C.

(a) If the initial concentration is 1.65×10^{-2} mol dm^{-3}, what is the concentration after 825 s?

(b) How long would it take for the concentration of N_2O_5 to decrease to 1.00×10^{-2} mol dm^{-3} from its initial value, given in (a)?

Testing for a rate law

Plot [A] vs *t*.



Example

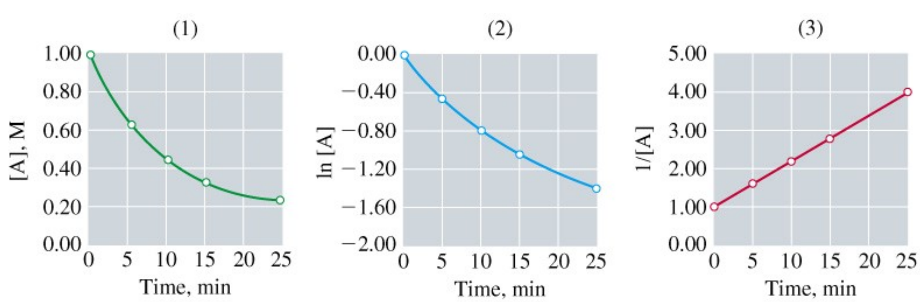
The data given below were obtained for the decomposition reaction, A → products.

(a) Establish the order of the reaction.

(b) What is the rate constant, k?

Time, min	[A],M	ln [A]	1/[A]
0	1.00	0.00	1.00
5	0.63	−0.46	1.6
10	0.46	−0.78	2.2
15	0.36	−1.02	2.8
25	0.25	−1.39	4.0

Solution



Reaction Mechanisms

- elementary process – one-step reaction
- mechanism – entire series of elementary processes
- The rate law for an elementary process can be predicted.

$$NOCl + Cl \rightarrow NO + Cl_2$$
$$rate = k[NOCl][Cl]$$

$$2NO_2 \rightarrow NO_3 + NO$$
$$rate = k[NO_2]^2$$

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

This is a stoichiometric (balanced) equation that describes the **overall** result of a reaction.

The mechanism describes how this overall process occurs in terms of elementary steps.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

1. $N_2O_5(g)$ 🕓 $NO_2(g) + NO_3(g)$
2. $NO_2(g) + NO_3(g) \rightarrow NO_2(g) + O_2(g) + NO(g)$
3. $NO(g) + NO_3(g) \rightarrow 2NO_2(g)$

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

overall reaction

- Steps 1 – 3 are elementary steps. Together they constitute the mechanism of the reaction.

Molecularity

- molecularity – the number of reactant particles involved in an elementary reaction.
  - unimolecular
  - bimolecular
  - termolecular

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

1. $N_2O_5(g)$ ⌚ $NO_2(g) + NO_3(g)$

   unimolecular →

   bimolecular ←

2. $NO_2(g) + NO_3(g) \rightarrow NO_2(g) + O_2(g) + NO(g)$

   bimolecular

3. $NO(g) + NO_3(g) \rightarrow 2NO_2(g)$

   bimolecular

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

overall reaction

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

- By **experiment** the above reaction is **first order overall**, i.e. rate = $k[N_2O_5]^1$, and the mechanism is consistent with this.

- A mechanism is made up of a series of elementary steps each of which refers to a distinct process which occurs in the overall reaction.
- Thus reaction 2 refers to an actual collision between an NO_2 and an NO_3 molecule.
- An overall equation says nothing about the mechanism.

- A mechanism is constructed from experimental investigations. The most important of these are investigations concerning the order of the reaction.
- Note – overall reactions **do not** have molecularity – only elementary reactions have molecularity.

Collision Theory

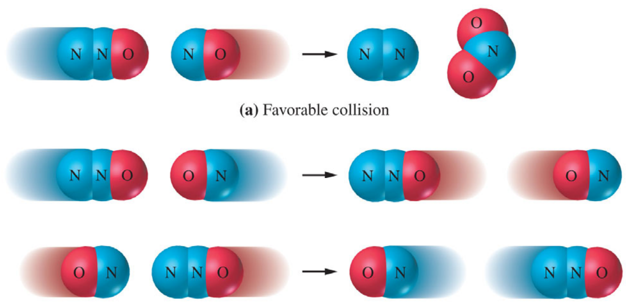
- For two molecules to react in the gas phase they must first collide.
- **But** not all collisions result in reaction!!!

Collision frequency

- The rate of reaction depends on the number of collisions per second. (The number of collisions varies with temperature and concentration.)
- The collision frequency varies only slowly with temperature (2% increase for 10 °C rise in temperature).

Correct Orientation (steric factor)

- Not all collisions are reactive because each collision has to be between correctly oriented molecules.



(a) Favorable collision

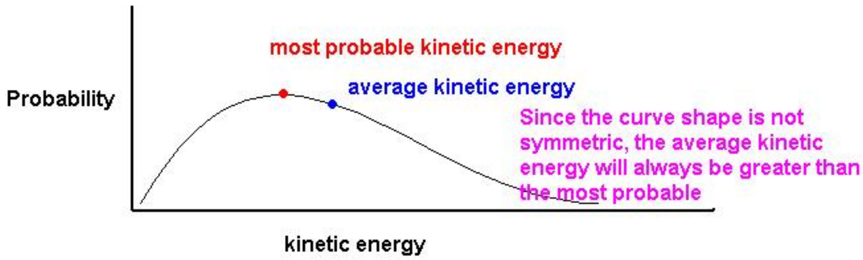
(b) Unfavorable collisions

Correct Energy

- Also each collision has to be of sufficient energy to break bonds etc. in the reaction, i.e. only a certain fraction of all collisions are reactive.

Energy Distribution

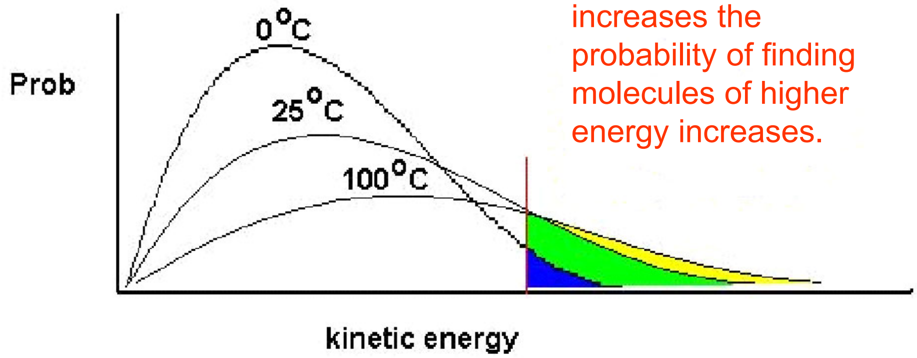
- In the gas phase molecules have different speeds (and hence kinetic energy) and the diagram shows how many (what fraction of) molecules have what kinetic energies (Maxwell distribution law).



Energy and Temperature

- Since the velocity of molecules increases with temperature so does their kinetic energy. An increase in their energy results in an increase in the number of reactive collisions. Hence the rate of reaction increases.

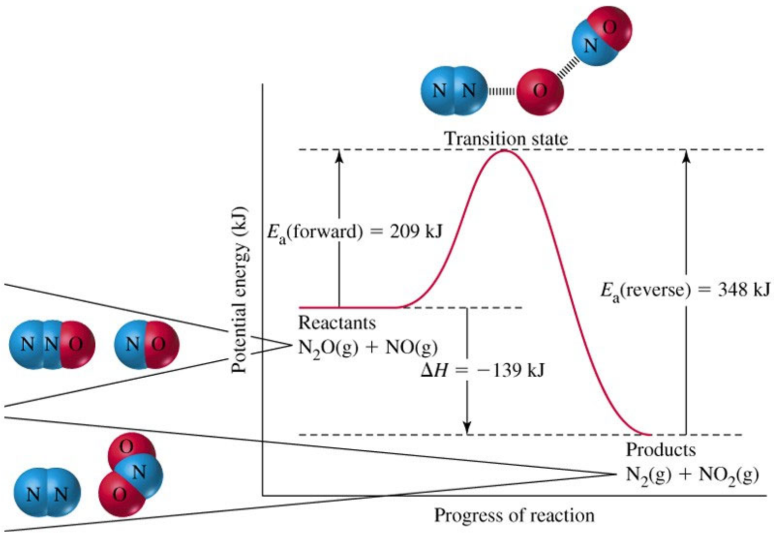
Energy and Temperature



As temperature increases the probability of finding molecules of higher energy increases.

- If the molecules require a certain kinetic energy to react then the fraction with that energy is indicated by the shaded portions in the above diagram.
- For this fraction of molecules the collisions will be reactive.
- Notice how this fraction increases with temperature.

$N_2O + NO$ 🕓 $N_2 + NO_2$



The Arrhenius Equation

- The **Arrhenius equation** describes the way in which a reaction rate changes with temperature.

$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

Symbols in the Arrhenius Equation

- A ≡ pre-exponential factor or frequency factor – this is the collision rate and is effectively temperature independent.
- E_a ≡ activation energy – this is the energy the molecules require to make a collision reactive.
- k ≡ rate constant – characteristic of a specific reaction, indicates the fraction of successful collisions at a given temperature, varies with temperature (as above), for fast reactions k is large, for slow reactions k is small.

$$k = Ae^{-E_a/RT}$$

- The Maxwell-Boltzmann distribution tells us that the fraction of molecules with energy greater than a value E_a is given by

$$\frac{N}{N_{total}} = e^{-E_a/RT}$$

$$k = Ae^{-E_a / RT}$$

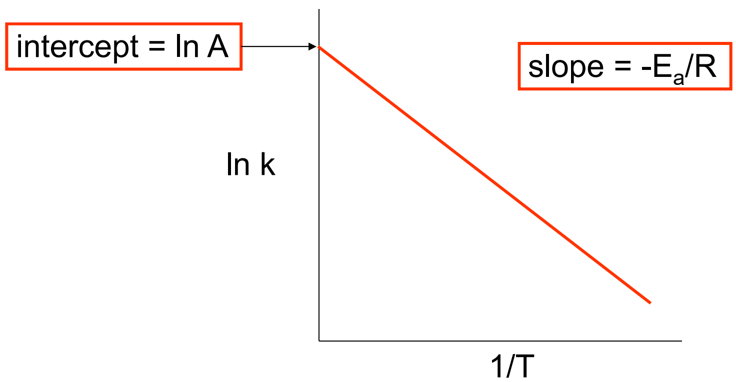
- Hence the rate constant ($k = Ae^{-E_a / RT}$) is given by the total number of collisions per second (A) multiplied by the fraction of those collisions which involve molecules with sufficient energy to react ($e^{-E_a / RT}$).

Plotting the Arrhenius Equation

- If k for a reaction is plotted against 1/T, E_a and A are obtained from the slope and intercept respectively.

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$$

Arrhenius Plot



Example

The rate constant for the formation of hydrogen iodide from the elements

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is 2.7×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$ at 600 K and 3.5×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ at 650 K.

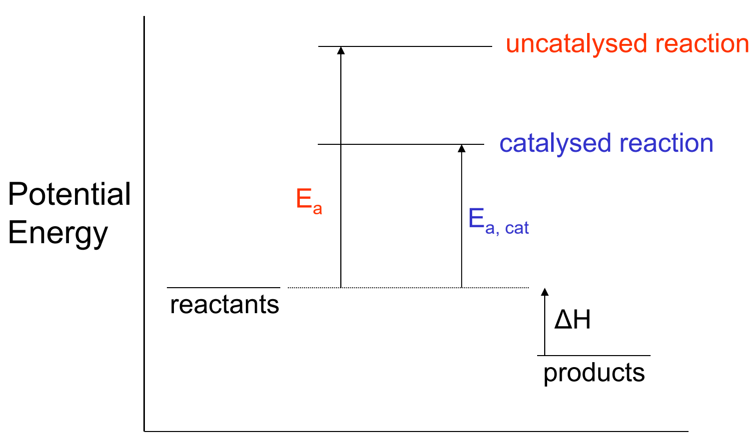
(a) Find the activation energy.

(b) Calculate the rate constant at 700 K.

Catalysts

- This is a substance that increases the rate of a chemical reaction without itself being used up.
- It participates by changing the mechanism of the reaction. It provides a path with lower activation energy than the uncatalyzed reaction.
- If the activation energy is smaller, a greater fraction of molecules will have the minimum energy to react.

Potential Energy Diagram



Types of catalysts

- homogeneous catalysts – exist in same phase as reactants
- heterogeneous catalysts – exist in a separate phase

Homogeneous Catalysis

- An example is the lead chamber process for making H_2SO_4

	$S + O_2 \rightarrow SO_2$	burn S
slow reaction	$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$	oxidation
	$SO_3 + H_2O \rightarrow H_2SO_4$	dissolve in H_2O

- In presence of NO_2

$NO_2 + SO_2 \rightarrow NO + SO_3$	NO_2 oxidises
$NO + \frac{1}{2}O_2 \rightarrow NO_2$	NO reoxidised

- NO_2 provides a lower energy path.

Heterogeneous Catalysis

- A heterogeneous catalyst promotes a reaction on its surface. The reactant molecule is adsorbed on the surface of the catalyst where interaction with the surface increases reactivity. For example,

  $3H_2 + N_2 \rightarrow 2NH_3$ NH_3 for fertilizer

- The surface of the Fe catalyst contains traces of Al and K oxides. H_2 and N_2 molecules dissociate while being held on catalytic surface. H atoms then combine with N atoms to form NH_3. NH_3 breaks away freeing surface sites for further reaction.
- If something blocks the active sites it poisons the surface by destroying the catalytic properties.

$$2CO + 2NO \xrightarrow{Rh} 2CO_2 + N_2$$