

- Basics of rate laws;
- Complex reactions: consecutive and parallel reactions;
- Temperature dependence of reaction rates;
- Reaction mechanisms: steady-state approximation, pre-equilibria, unimolecular reactions;
- Catalysis

Reference Text Books:

- Peter Atkins and Julio De Paula, Elements of Physical Chemistry, 7th/8th/10th editions
- Robert J. Silbey, Robert A Alberty and Moungi G Bawendi, Physical Chemistry, 7th edition
- Ira N Levine, Physical Chemistry, 6th edition
- Nivaldo J. Tro, Chemistry, A Molecular Approach, 4th edition

- **Chemical Kinetics:** Study of the effects of various factors on reaction rate.
- **Reaction rate:** How fast a reaction occurs is measured by the reaction rate



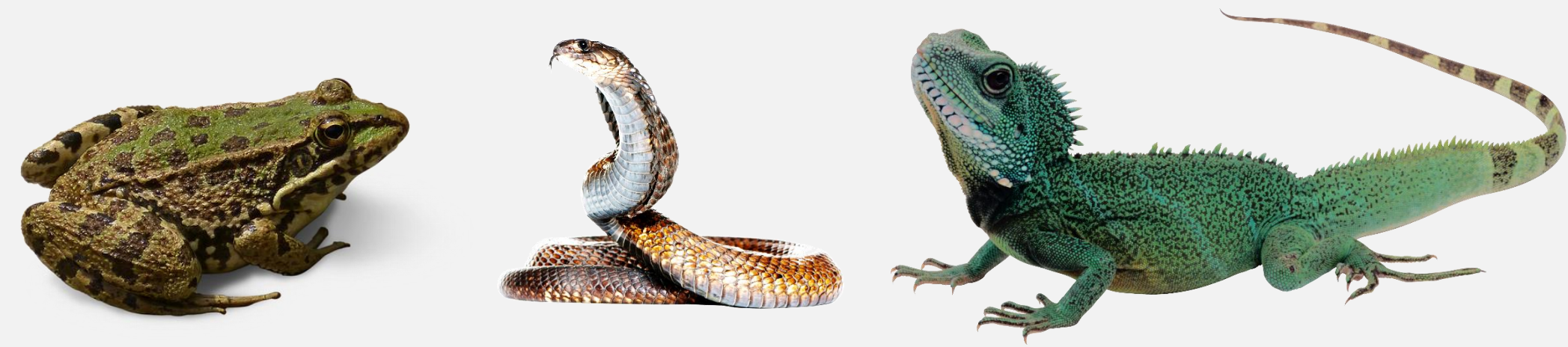
Three kinds of factors:

- (i) [A], [B], [Y] , [Z] and Catalyst
- (ii) Temperature and Pressure
- (iii) External fields such as electric field, magnetic field and light

Basics of Chemical Kinetics

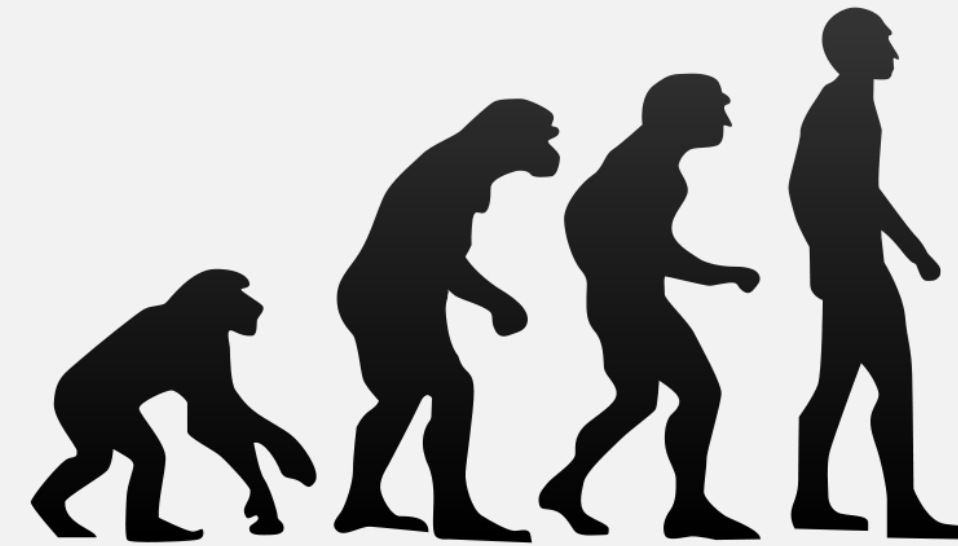
- **Ectotherm:** Relies on external heat sources to control its body temperature

Examples: Frogs, snakes and lizard



- **Endotherm:** Can regulate its internal body temperature based on heat produced within the body

Examples: Mammals



- A drop in temperature in cold seasons immobilizes reptiles (snakes or lizards) because their movement depends on the chemical reactions which occur within their muscles
- The rates of these reactions are very sensitive to the temperature

- The reactions that produce muscle movement become slow when T decreases
- “ “ “ fast when T increases

- That is why when reptiles are exposed to cold weather, they become lethargic and are unable to move quickly
- Because of this they try to stay in places where temperature change is in narrow range (shade)

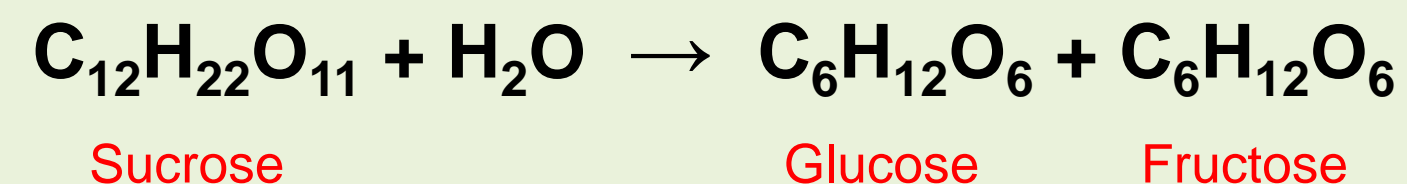
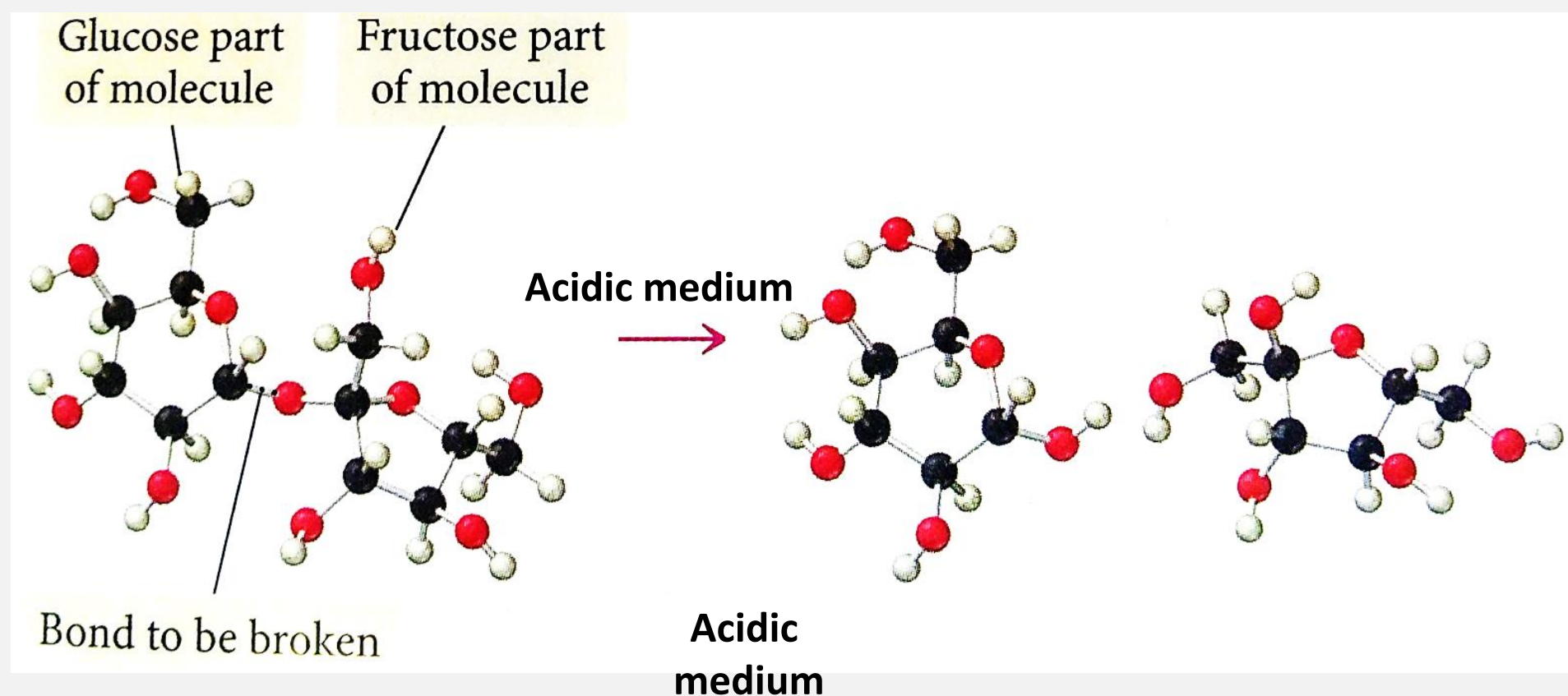
Basics of Chemical Kinetics

- *A successful launch of a rocket depends on the rate at which the fuel burns*
- *If the fuel burns too fast, the rocket can explode*
- *If it burns too slowly, then rocket may not even leave the ground*



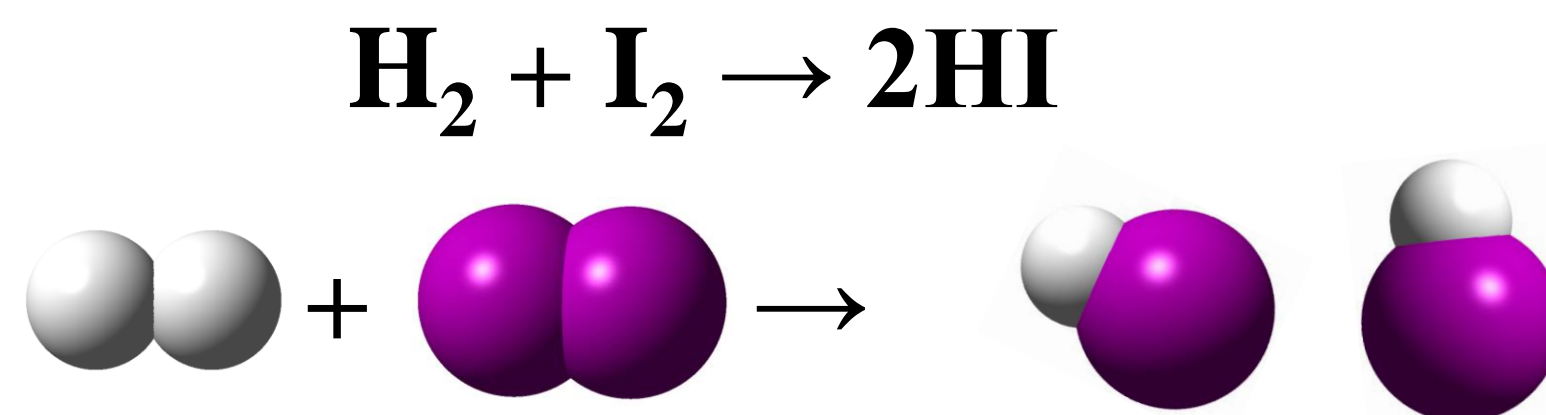
Reaction rate is very important!!!

- **Ludwig Wilhelmy (1812-1864) was the first one to measure reaction rate of following reactions**



- *Hydrolysis of sucrose, in presence of acid, breaks it into glucose and fructose*
- *Reaction time was observed to be several hours*
- **Wilhelmy also showed that rate of the reaction depended greatly on the initial amount of sugar; greater the initial amount, the faster was the initial rate**

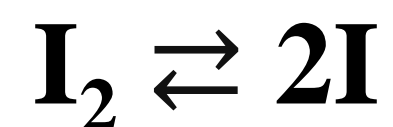
- **Elementary Reaction:** Products are formed from reactants by only one single step and no intermediate is detected from macroscopic experimental methods
- **Complex/Composite Reactions:** A reaction involving two or more elementary reactions



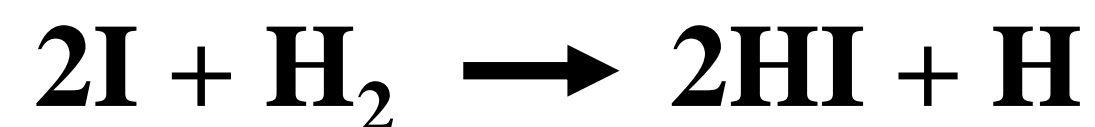
This reaction was originally thought to be elementary. But, in reality it occurs in more than one step

- **Reaction Mechanism:** Sequence of elementary reactions is called reaction mechanism of a complex reaction

In one of the proposed mechanisms for the above reaction, following elementary steps are involved:

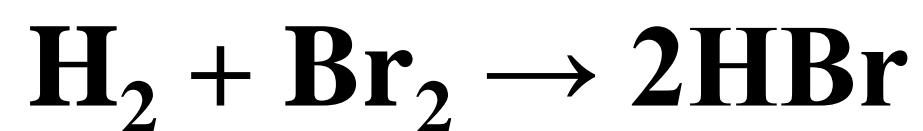


Dissociation of Iodine (fast, equilibrium)

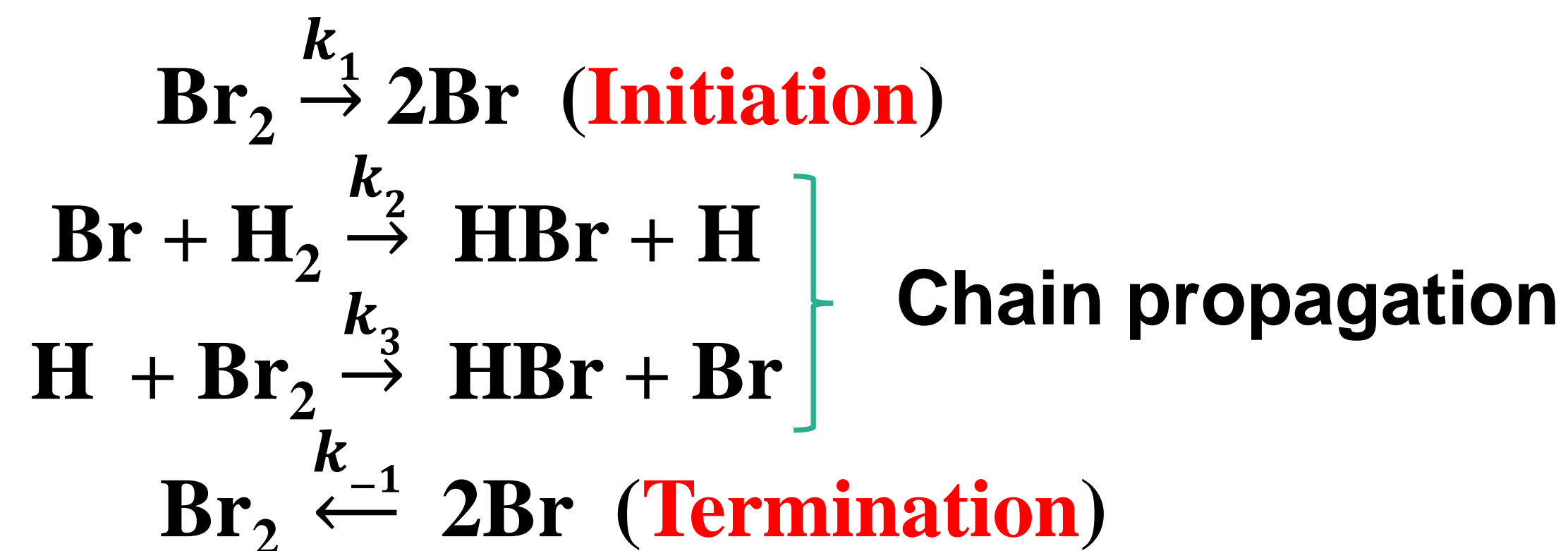


Combination (slow)

- **Chain Reactions:** Involves repetition of a cycle of reactions such that certain reaction intermediates consumed in one step are regenerated in another.
- The intermediates may be atoms, free radicals or ions.



If in the above reaction, **HBr** is removed as fast as it is formed, the process is believed to be as follows



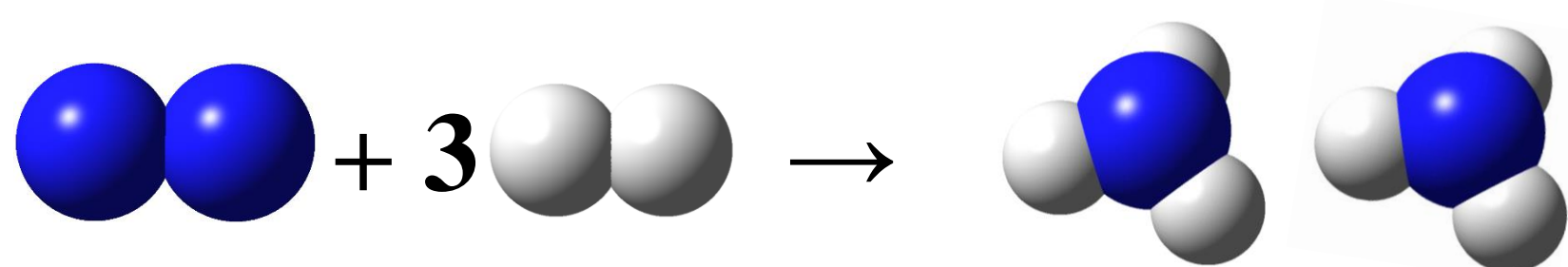
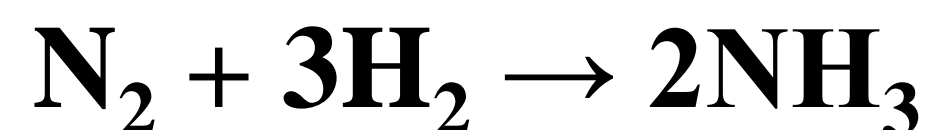
Reaction Stoichiometry

• General expression of a chemical reaction of known stoichiometry

$$0 = \sum_i \nu_i B_i$$

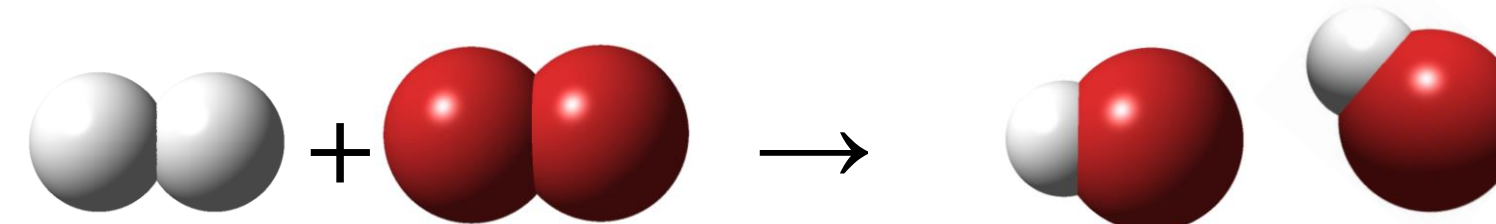
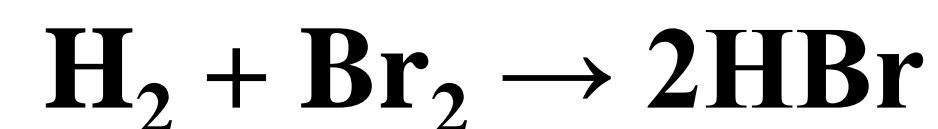
B_i represents reactants or products and ν_i is the corresponding stoichiometric coefficient

• **Stoichiometric Coefficient (ν):** *-ve* for reactants and *+ve* of products; *-a* for **A**, *-b* for **B**, *y* for **Y** and *z* for **Z** in a general reaction of type $a\mathbf{A} + b\mathbf{B} + \dots \rightarrow \dots y\mathbf{Y} + z\mathbf{Z}$



$$0 = 2\text{NH}_3 - \text{N}_2 - 3\text{H}_2$$

$$\nu(\text{N}_2) = -1, \nu(\text{H}_2) = -3, \nu(\text{NH}_3) = 2$$



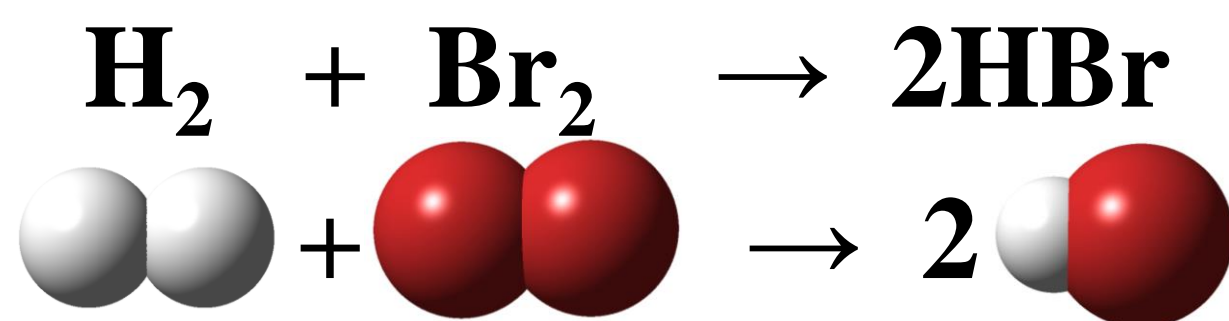
$$0 = 2\text{HBr} - \text{H}_2 - \text{Br}_2$$

$$\nu(\text{H}_2) = -1, \nu(\text{Br}_2) = -1, \nu(\text{HBr}) = 2$$

Reaction Stoichiometry

- **Time-independent stoichiometry:** An overall stoichiometric equation applies throughout the course of the reaction, no significant intermediate is formed

Example:



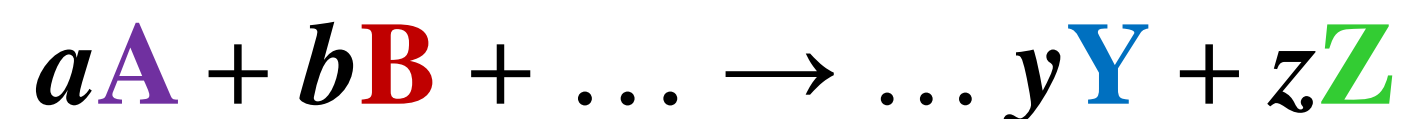
$$v(\text{H}_2) = -1, v(\text{Br}_2) = -1, v(\text{HBr}) = 2$$

t=0	$n_{\text{H}_2}^0$	$n_{\text{Br}_2}^0$	n_{HBr}^0
t	n_{H_2}	n_{Br_2}	n_{HBr}

$$\frac{n_{\text{H}_2} - n_{\text{H}_2}^0}{-1} = \frac{n_{\text{Br}_2} - n_{\text{Br}_2}^0}{-1} = \frac{n_{\text{HBr}} - n_{\text{HBr}}^0}{2}$$

← This equality holds during the course of the reaction

• In general:



$$\frac{n_{\text{A}} - n_{\text{A}}^0}{-a} = \frac{n_{\text{B}} - n_{\text{B}}^0}{-b} = \dots = \frac{n_{\text{Y}} - n_{\text{Y}}^0}{y} = \frac{n_{\text{Z}} - n_{\text{Z}}^0}{z}$$

Reaction Stoichiometry

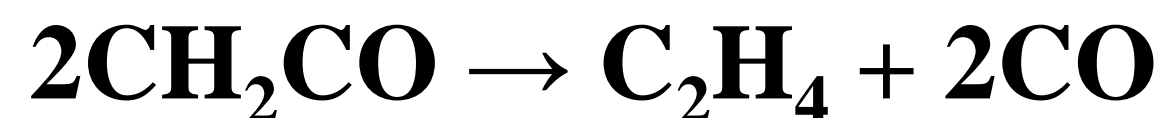
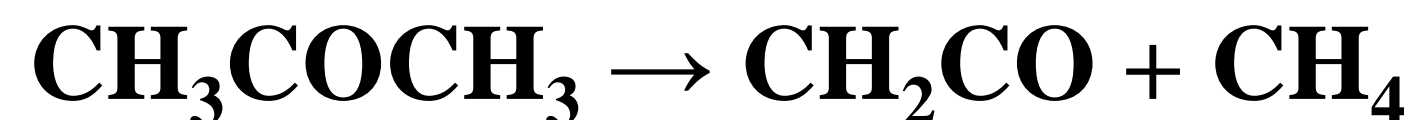
- **Time-dependent stoichiometry:** The stoichiometry of the species involved changes throughout the course of the reaction

Example: Thermal decomposition of acetone



$$\frac{n_{\text{CH}_3\text{COCH}_3} - n_{\text{CH}_3\text{COCH}_3}^0}{-2} = \frac{n_{\text{CH}_4} - n_{\text{CH}_4}^0}{2} = \frac{n_{\text{C}_2\text{H}_4} - n_{\text{C}_2\text{H}_4}^0}{1} = \frac{n_{\text{CO}} - n_{\text{CO}}^0}{2} \quad \text{does not apply}$$

- It is observed that appreciable amount of ketene (CH_2CO) are present during the course of the reaction.
- Following processes also occur during the reaction:



- Thus, the amounts of the products present during the course of the reaction are not related by any stoichiometric equation to the amounts of the reactants that have been consumed.

Convention for writing the reactions or stoichiometric equations

- When emphasis is on equilibrium state



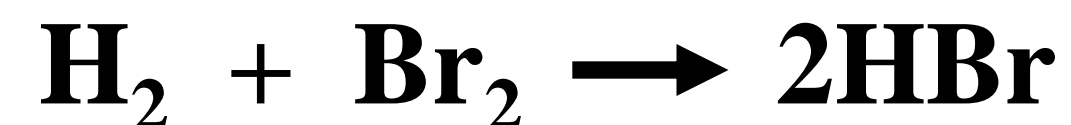
- When the reaction is occurring in a single direction



- When there is a interest in the kinetics of the reaction in both directions



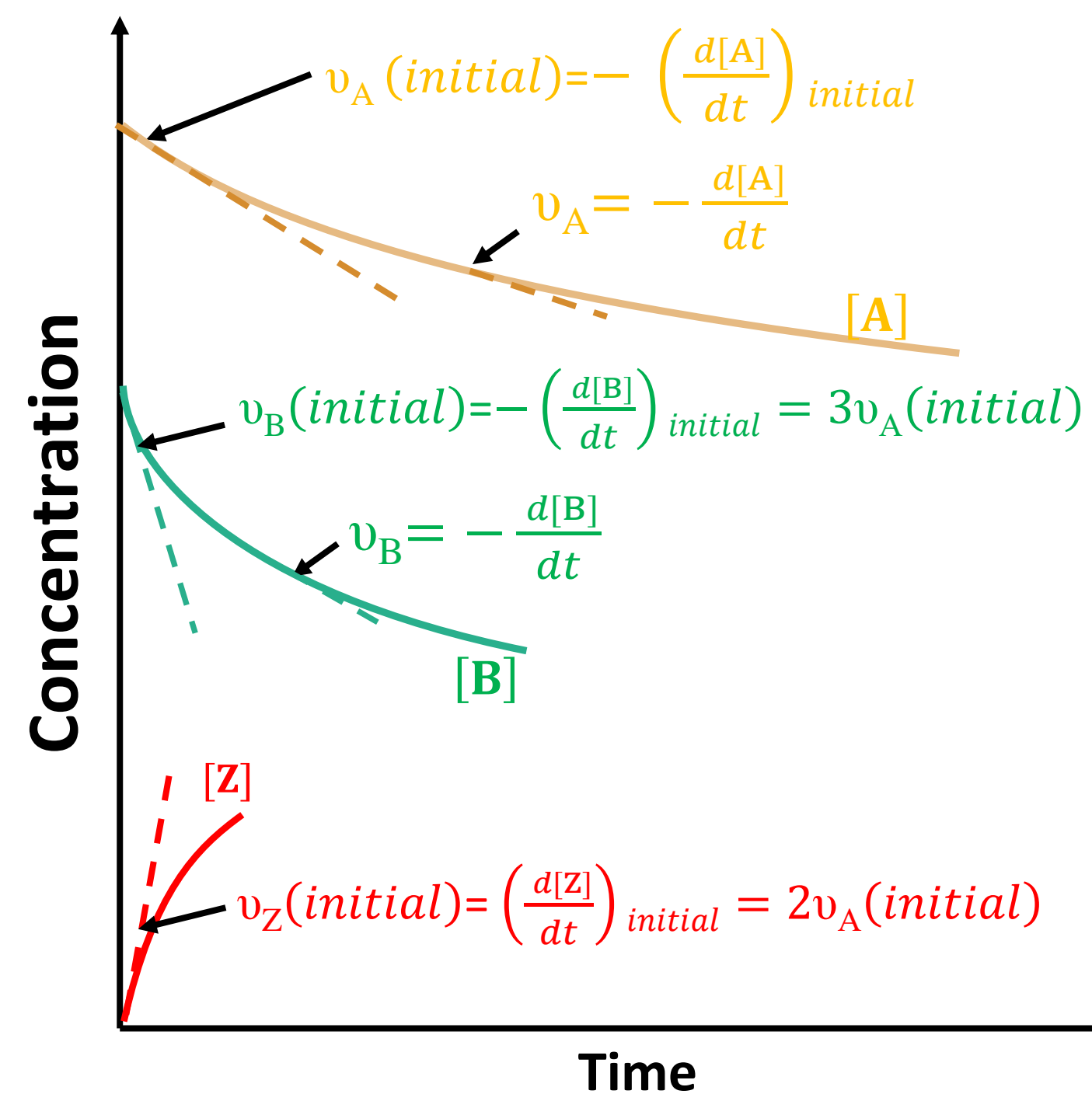
- For elementary reaction



Rates of Consumption and Formation



t=0	$[\text{A}]_0$	$[\text{B}]_0$	0
t	$[\text{A}]$	$[\text{B}]$	$[\text{Z}]$



• Rate of consumption of reactant A

$$v_A = - \frac{d[\text{A}]}{dt}$$

• Rate of formation of product Z

$$v_Z = \frac{d[\text{Z}]}{dt}$$

• Since the stoichiometric coefficients are different for the three species, the rates of change of their concentrations will also be different. They are related by the following relation:

$$v_A = \frac{1}{3} v_B = \frac{1}{2} v_Z$$

Unit: mol m⁻³ s⁻¹ or mol dm⁻³ s⁻¹ or mol cm⁻³ s⁻¹

• Note that the rates of consumption of the reactants are different than rate of formation of the product! Slopes are different!

Extent of Reaction (ξ) [T. De Donder, 1922]

- For any reactant or product in a reaction having time-independent stoichiometry, the extent of reaction (ξ) is defined as

$$n = n^0 + \nu \xi$$

$$\xi = \frac{n - n^0}{\nu}$$

Pronounced as “Xi” \longrightarrow

n^0 is the initial amount of the substance

n is the amount of the substance at time t

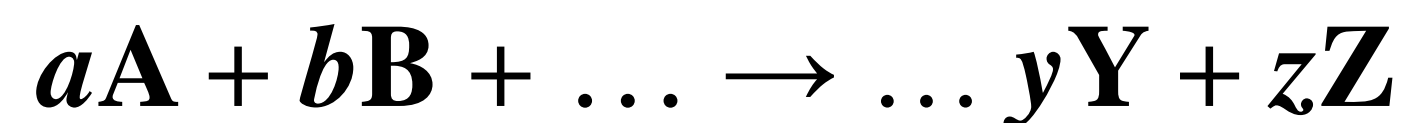
ν is the stoichiometric coefficient for the species for the particular equation written down for the reaction

- The interesting fact is that ξ is same for every reactant and product

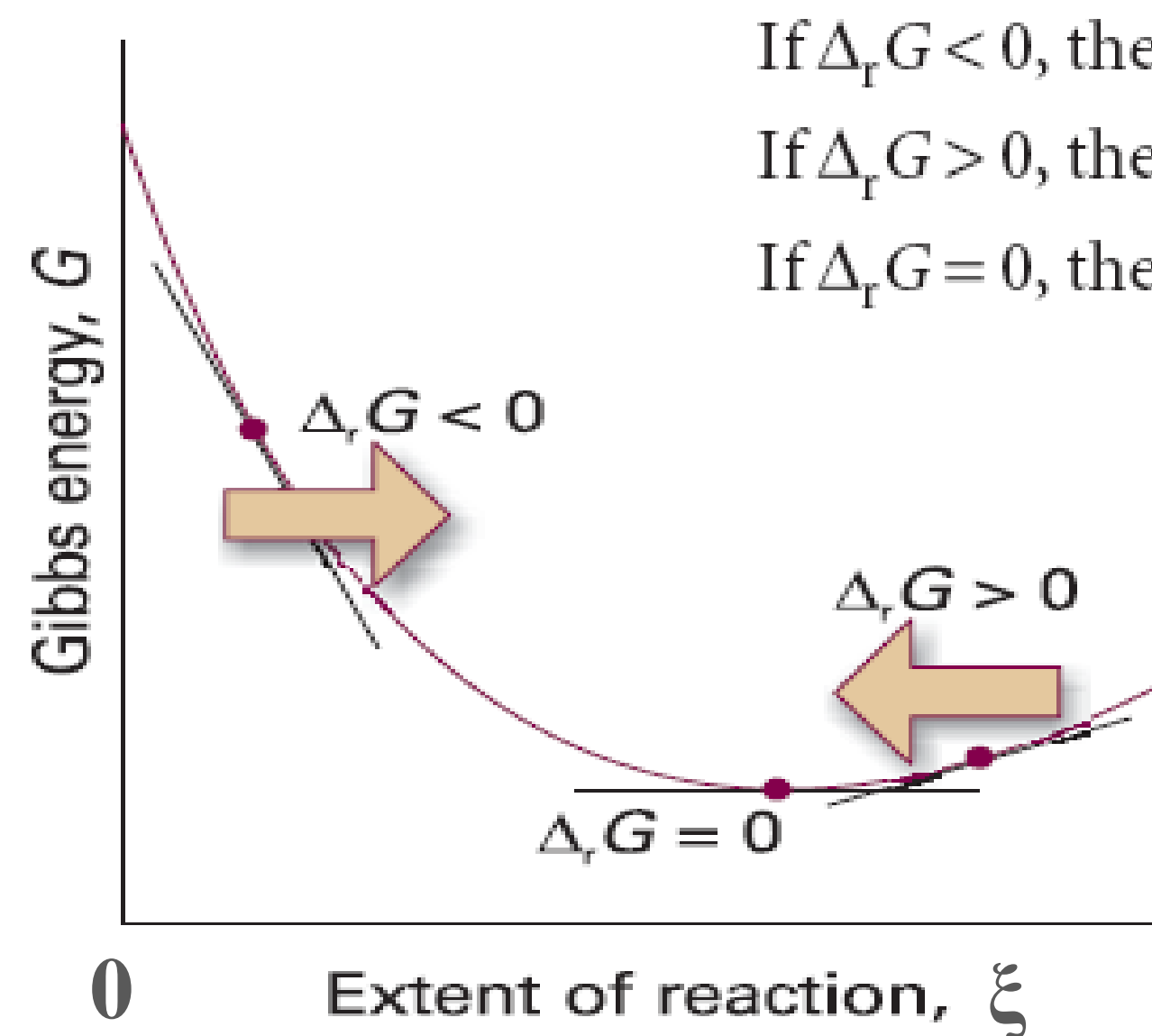
For any species i (reactant or product)

$$n_i = n_i^0 + \nu_i \xi$$

- For general equation:



$$\xi = \frac{n_A - n_A^0}{-a} = \frac{n_B - n_B^0}{-b} = \dots = \frac{n_Y - n_Y^0}{y} = \frac{n_Z - n_Z^0}{z}$$



If $\Delta_r G < 0$, the forward reaction is spontaneous.

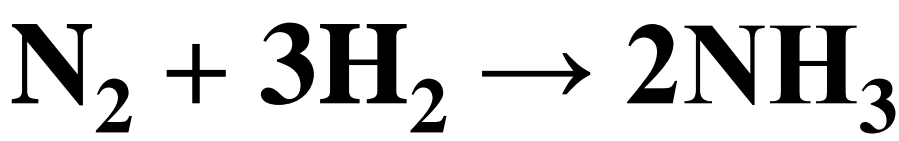
If $\Delta_r G > 0$, the reverse reaction is spontaneous.

If $\Delta_r G = 0$, the reaction is at equilibrium.

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{p,T}$$

Extent of Reaction (ξ)

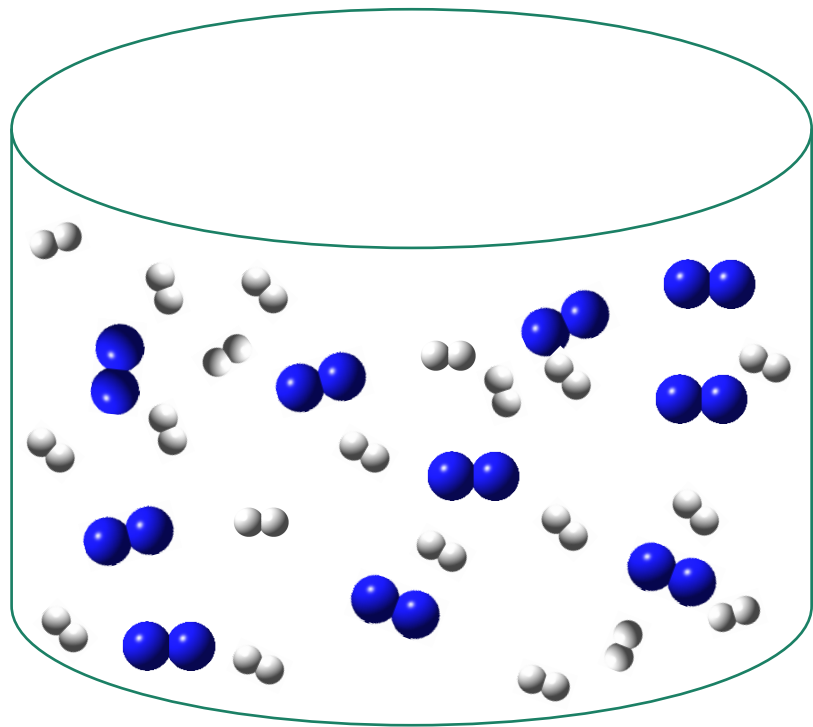
Example: 10.0 mol of N₂ and 20.0 mol of H₂ react to give 5.0 mol of NH₃ after certain time. If the stoichiometric equation is specified as



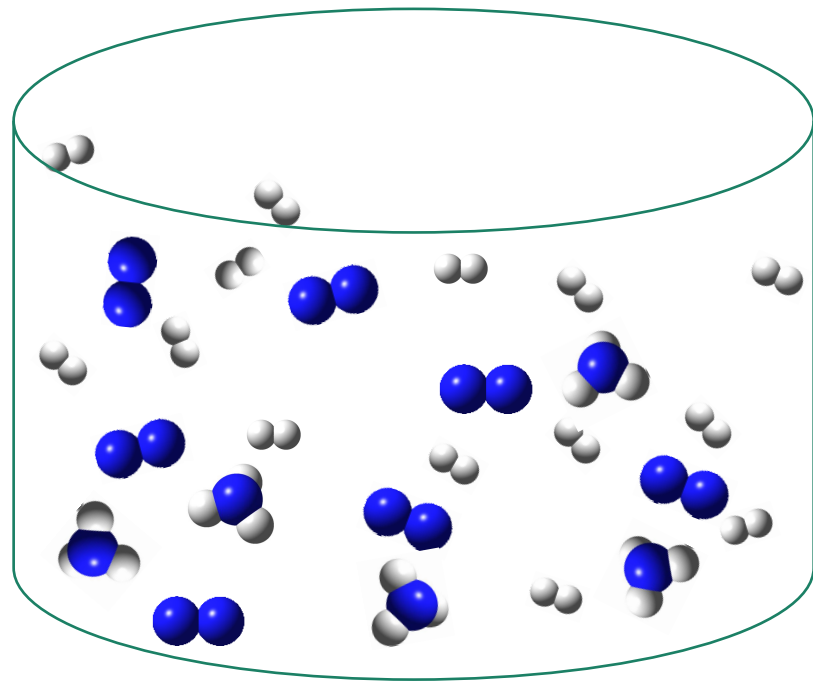
	N ₂	H ₂	NH ₃
Initial Amount (in mol)	10	20	0
Final Amount (in mol)	7.5	12.5	5.0
$n - n^0$ (in mol)	-2.5	-7.5	5.0
Stoichiometric coefficient ν	-1	-3	2
ξ (in mol)	2.5	2.5	2.5

If the stoichiometric equation was $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$, then

Stoichiometric coefficient ν	-1/2	-3/2	1
ξ (in mol)	5	5	5



Initial



Final

Rate of Reaction (\mathfrak{v})

- Rates of consumption and formation are not the same in general for all the species involved in a chemical reaction
- Desirable to define a rate which is same for all the species for a given reaction
- Possible for a reaction showing time-independent stoichiometry

Rate of Reaction: $\mathfrak{v} = \frac{1}{V} \frac{d\xi}{dt} = \frac{\dot{\xi}}{V}$

For species i , $\dot{\xi} = \frac{1}{\nu_i} \frac{dn_i}{dt}$

$\dot{\xi}$ is also called rate of conversion

$$\mathfrak{v} = \frac{1}{\nu_i V} \frac{dn_i}{dt}$$

V is the volume of the system

- For the general reaction, $aA + bB + \dots \rightarrow \dots yY + zZ$

$$\mathfrak{v} = -\frac{1}{aV} \frac{dn_A}{dt} = -\frac{1}{bV} \frac{dn_B}{dt} = \frac{1}{yV} \frac{dn_Y}{dt} = \frac{1}{zV} \frac{dn_Z}{dt}$$