KINETICS OF HOMEGENOUS REACTIONS

A. SARATH BABU

During a chemical reaction

$$aA + bB \rightarrow rR + sS$$

- ★ Overall Mass is conserved
- ★ Is mass with respect to a species conserved?
- ★ The mass of a reactant depletes / disappears when a reaction is in progress.
- ★ The mass of a product increases/appears when a reaction is in progress

Rate of Reaction:

$$aA + bB \rightarrow rR + sS$$

- Rate of reaction is defined with respect to a species participating in the reaction
- Rate of formation of species i (r_i)

$$r_i = \frac{Moles\ of\ i\ formed}{(unit\ time)(unit\ volume)} = \frac{moles}{(s)(m^3)}$$

- If i is a product, moles of product get formed and hence the rate is +ve
- If i is a reactant, moles of reactant get consumed and hence the rate is -ve

- To avoid dealing with both +ve and –ve rates
- If i is a product, the rate is defined in terms of rate of appearance (r_i)
- If i is a reactant, the rate is defined in terms of disappearance ($-r_i$)

$$d\xi = \frac{dn_i}{\nu_i}$$

$$-r_A = \frac{Moles\ of\ \ A\ disappeared}{(unit\ time)(unit\ volume)} = \frac{-1}{V}\frac{dN_A}{dt} = \frac{-\nu_A}{V}\frac{d\xi}{dt}$$

$$r_R = \frac{Moles\ of\ \ R\ appeared}{(unit\ time)(unit\ volume)} = \frac{1}{V}\frac{dN_R}{dt}$$

✓ It may be noted that:

rate of disappearance = - (rate of appearance)

For the Reaction: aA + bB → rR + sS

- Can we have different Rates for the same reaction at the same time
- How the change in moles of different species related at a given time?

$$\frac{-dN_A}{a} = \frac{-dN_B}{b} = \frac{dN_R}{r} = \frac{dN_S}{s}$$

- How are rates of different species related?

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

Example: A + 2B → 2C

Molecularity of a reaction refers to the min. no. of molecules which must combine

Law of mass action: The rate of a reaction is proportional to the product of active masses of the reactants, where the active masses are raised to the power of their respective stoichiometric coefficients.

$aA + bB \rightarrow rR + sS$

$$-r_A = kC_A^a C_B^b$$

The second part is true for ideal solution behavior.

Order of a reaction

$$-r_A = kC_A^a C_B^b C_R^r \ldots$$

- Overall Order n = a + b + r + . . .
- Order w.r.t. A = a; Order w.r.t. B = b

Without rate law, order cannot be identified

$$-r_A = \frac{k_1[H_2][Br_2]^{1/2}}{k_2 + [HBr]/[Br_2]}$$

Order n = ??

Elementary reaction ??

Order & Molecularity for Elementary reactions

$$\text{Unimolecular} \quad A \rightarrow \text{Prod.} \quad -r_A = kC_A$$

$$\text{Bimolecular} \quad 2A \rightarrow \text{Prod.} \quad -r_A = kC_A^2$$

$$\text{Bimolecular} \quad A + B \rightarrow \text{Prod.} \quad -r_A = kC_A C_B$$

$$\text{Trimolecular} \quad 3A \rightarrow \text{Prod.} \quad -r_A = kC_A^3$$

$$\text{Trimolecular} \quad 2A + B \rightarrow \text{Prod.} \quad -r_A = kC_A^2 C_B$$

$$\text{Trimolecular} \quad A + B + C \rightarrow \text{Prod.} \quad -r_A = kC_A C_B C_C$$

Order & Molecularity of the forward reaction can be different from those of the backward reaction

Elementary reaction

- obeys the law of mass action
- proceeds in one step

Non-Elementary reaction

- does not obey the law of mass action
- proceeds in more than one step
- involves the appearance of intermediates

Example: $H_2 + Br_2 \rightarrow 2HBr$

$$-r_A = \frac{k_1[H_2][Br_2]^{1/2}}{k_2 + [HBr]/[Br_2]}$$

What is the order & molecularity ??

Non-Elementary reaction

- Non-Elementary reactions involve more than one step
- Involve the formation of intermediates
- Intermediates cannot be observed as they are highly reactive and present in minute quantities
- Intermediates could be:
    - Free radicals: CH_3^*, $C_2H_5^*$ etc.
    - Ions & Polar substances: Na^+, OH^-,NH_4^+
    - Highly reactive molecules: $A \rightarrow R \rightarrow S$
    - Transition State Complexes

Searching the reaction mechanism for Non-Elementary reactions

1. Assume an active intermediate
2. Postulate a mechanism using the experimental rate law
3. Model each step in the reaction mechanism as elementary reaction
4. $r_{i,\ net} = \sum r_i$ all elementary steps
5. Use PSSH (SSA): The net rate of all active intermediates is zero
6. Eliminate the concentration of the intermediates
7. If the derived rate law does not agree with observed rate law from expt., goto (2)

Example: $(CH_3)_2N_2$ (Azomethane) → $C_2H_6 + N_2$

Mechanism:

$$A + A \Leftrightarrow A + A^*$$
$$A^* \rightarrow R + S$$

Solution:

1. Write the rate law for the desired compound

$$r_S = k_3[A^*]$$

2. Write the rate for the intermediate compounds

$$r_{A^*} = k_1[A]^2 - k_2[A^*][A] - k_3[A^*]$$

3. Use PSSH:

$$r_{A^*} = k_1[A]^2 - k_2[A^*][A] - k_3[A^*] = 0$$

$$k_1 [A]^2 = (k_2[A] + k_3)[A^*]$$

$$r_s = k_3[A^*] = \frac{k_1 k_3 [A]^2}{k_3 + k_2[A]}$$

- At low concentrations:

  $k_2[A] \ll k_3 \Rightarrow r_S = k_1[A]^2$ -- Second order

- At high concentrations:

  $k_2[A] \gg k_3 \Rightarrow r_S = (k_1 k_3/k_2)[A]$

  --- First order

Searching the reaction mechanism for Non-Elementary reactions – Thumb Rules

1. Species having the conc. appearing in the denominator of the rate law probably collide with the active intermediate

$$A + A^* \rightarrow \ldots$$

2. If a constant appears in the denominator, one of the steps could be the spontaneous decomposition of the intermediate

$$A^* \rightarrow \ldots$$

3. Species having the conc. appearing in the numerator of the rate law probably produce the active intermediate

$$A \rightarrow A^* + \ldots$$

Rate constant (Specific reaction rate):

The term reaction rate constant is actually a misnomer, since *k may vary with temperature,* the solvent for the reaction, and the concentrations of any catalysts that may be present in the reaction system. The term is in universal use, however, because it implies that the parameter *k* is independent of the concentrations of reactant and product species.

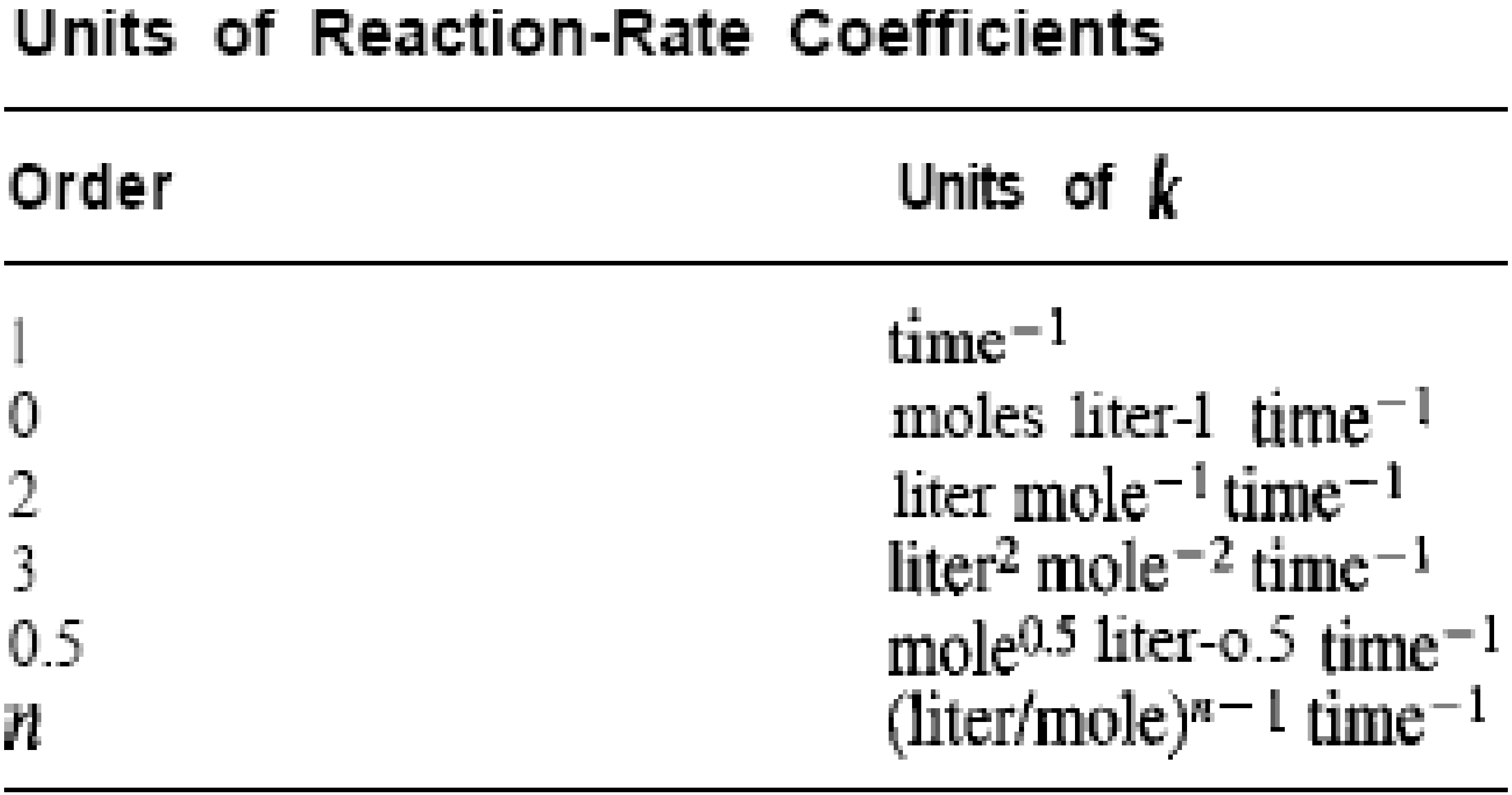
$$-r_A = \frac{1}{V}\frac{dN_A}{dt} = k(concentration)^n$$

$$k = (concentration)^{1-n}(time)^{-1}$$

Example: A + 2B → 2C

- Write the rate laws for each species ??
- Are the rate constants in each case same ?
- What is the relation between them??

$$\frac{k_{C_A}}{a} = \frac{k_{CB}}{b} = \frac{k_{CR}}{r} = \frac{k_{CS}}{s}$$



Units of Reaction-Rate Coefficients

Order	Units of k
1	time^{-1}
0	moles liter-1 time^{-1}
2	$\text{liter mole}^{-1}\ \text{time}^{-1}$
3	$\text{liter}^{2}\ \text{mole}^{-2}\ \text{time}^{-1}$
0.5	$\text{mole}^{0.5}$ liter-o.5 time^{-1}
n	$(\text{liter/mole})^{n-1}\ \text{time}^{-1}$

Lec, Stanislaw

Some like to understand what they believe in. Others like to believe in what they understand.

Kinetic view of equilibrium for Elementary reactions

$$A + B \Leftrightarrow C$$

Forward reaction rate = $k_1 C_A C_B$

Backward reaction rate = $k_2 C_C$

At equilibrium: Forward rate = Backward rate

$$k_1 C_A C_B = k_2 C_C$$

$$K_C = \frac{k_1}{k_2} = \frac{C_C}{C_A C_B}$$

Gas Phase reactions

$$A \rightarrow \text{Products}$$

$$-r_A = k_C C_A = k_p p_A = k_N N_A$$

What is the relation among different rate constants?

$$k_C = (RT)^n k_p = \left(\frac{RT}{P}\right)^n k_N$$

What is the relation among different Eq. constants?

$$K_C = (RT)^{-\Delta n} K_p = \left(\frac{RT}{P}\right)^{-\Delta n} K_N$$

Factors affecting the rate of reaction:

- ★ The nature of species involved in the reaction
- ★ Concentration of species
- ★ Temperature
- ★ Catalytic activity
- ★ Nature of contact of reactants
- ★ Wavelength of incident radiation

For Homogenous reactions:

Rate = f(Concentration, Temperature, Pressure)

- The functional form is known as the rate law and has to be obtained from experiment

Fractional Conversion (x_A):

$$x_A = \frac{moles\ of\ A\ converted}{Initial\ moles\ of\ A\ taken} = \frac{N_{A0} - N_A}{N_{A0}}$$

$$x_A = \frac{F_{A0} - F_A}{F_{A0}}\ (Flow\ Systems) \qquad x_A = \frac{C_{A0} - C_A}{C_{A0}}\ (Constant\ Density)$$

Extent of reaction (ξ):

$$d\xi = \frac{dn_i}{\nu_i} = -N_{A0}dx_A/\nu_A$$

The advantage of using ξ - unique rate of a given reaction.

The major drawback - ξ is an extensive variable and is proportional to the mass of the system.

The fractional conversion is an intensive measure of the progress of a reaction.

RELATIONSHIP BETWEEN CONVERSION, SELECTIVITY, AND YIELD

$$Y_R = \frac{\text{desired product formed}}{\text{reactant fed}}$$

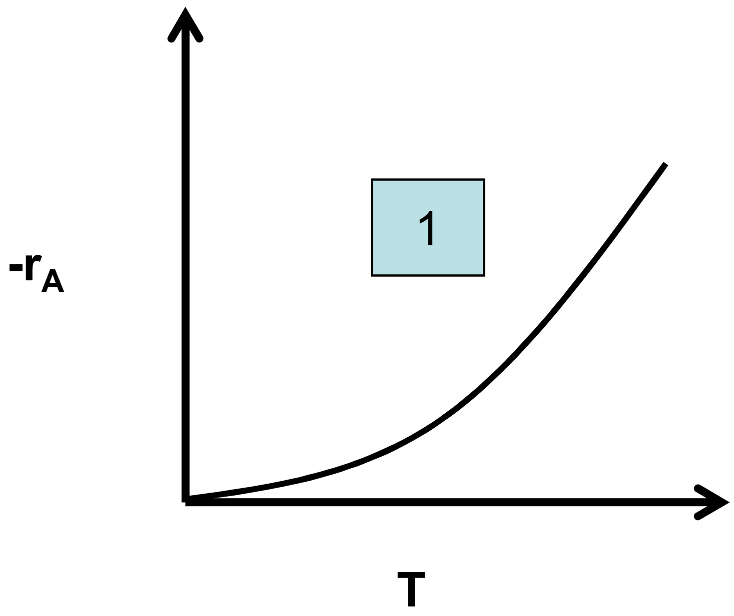
$$S_R = \frac{\text{amount of desired product}}{\text{amount of limiting reactant that has undergone chemical change}}$$

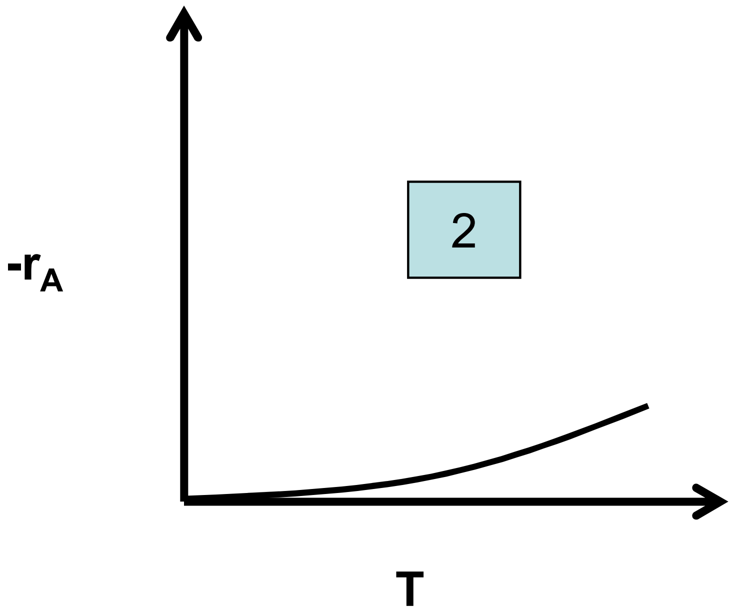
For the series $A \rightarrow B \rightarrow C$ and parallel reaction $A \rightarrow B$ $A \rightarrow C$, the selectivity of the wanted species B is

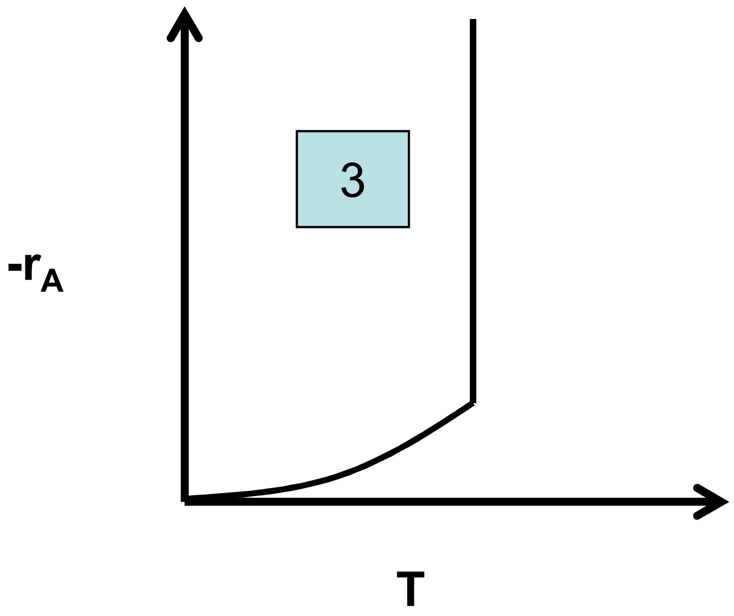
$$S_B = \frac{C_B}{C_{AO} - C_A} \qquad Y_B = \frac{C_B}{C_{AO}}$$

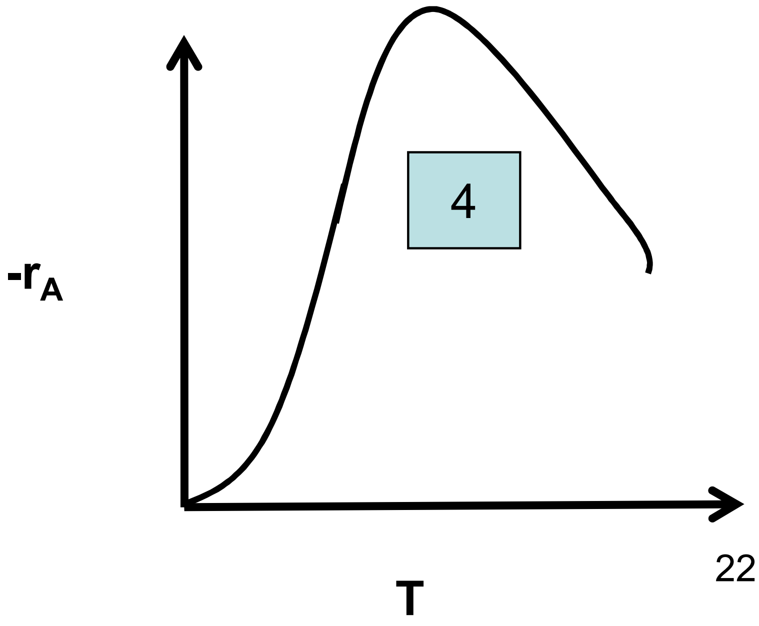
$$Y_B = \frac{C_B}{C_{AO}} = \left(\frac{C_B}{C_{AO} - C_A}\right)\left(\frac{C_{AO} - C_A}{C_{AO}}\right) = S_B \bullet X_B$$

Temperature dependency of Rate

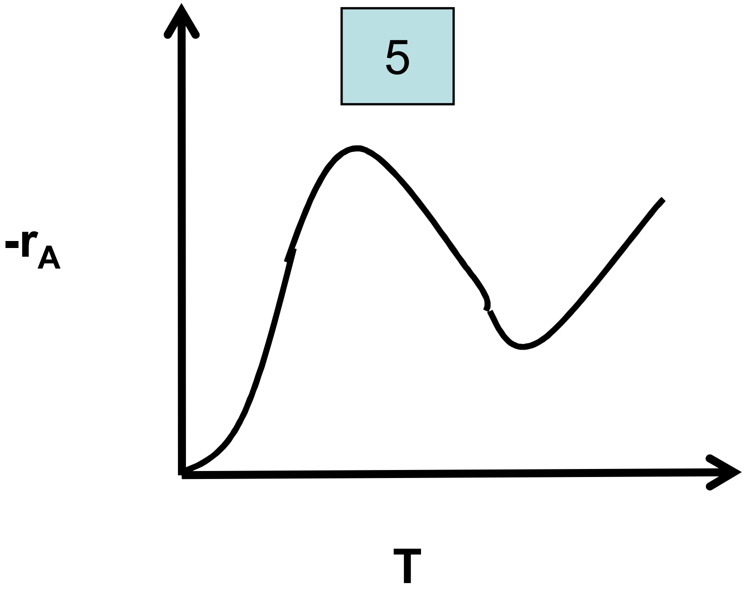


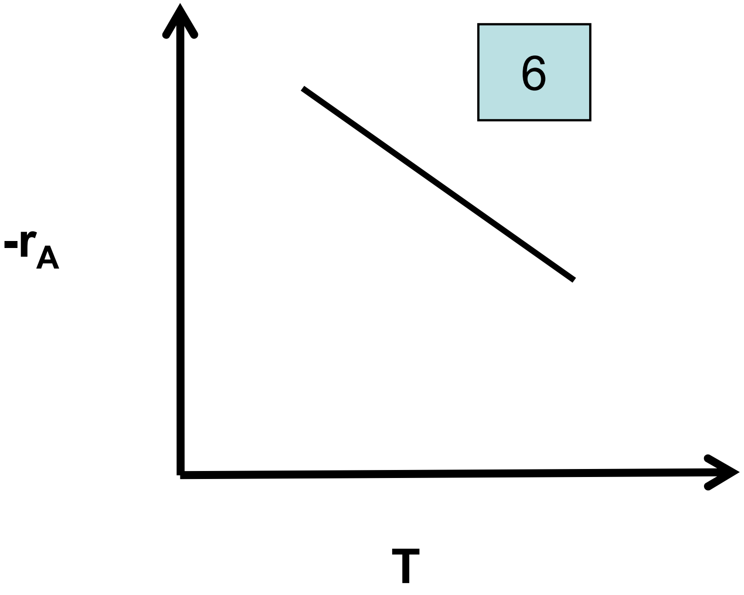




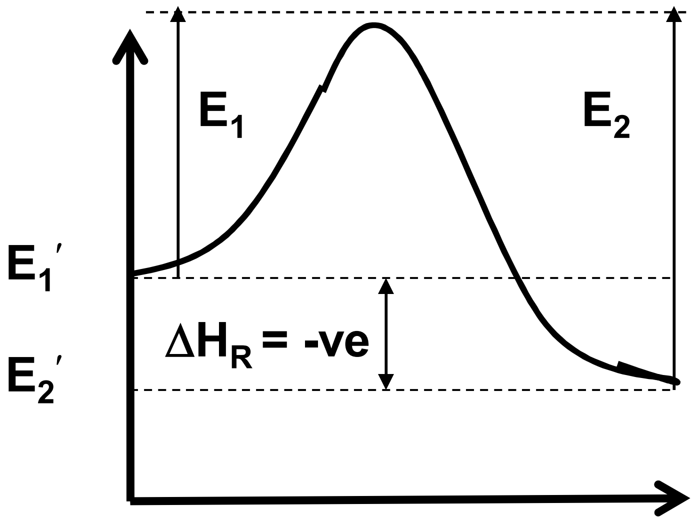


Temperature dependency of Rate



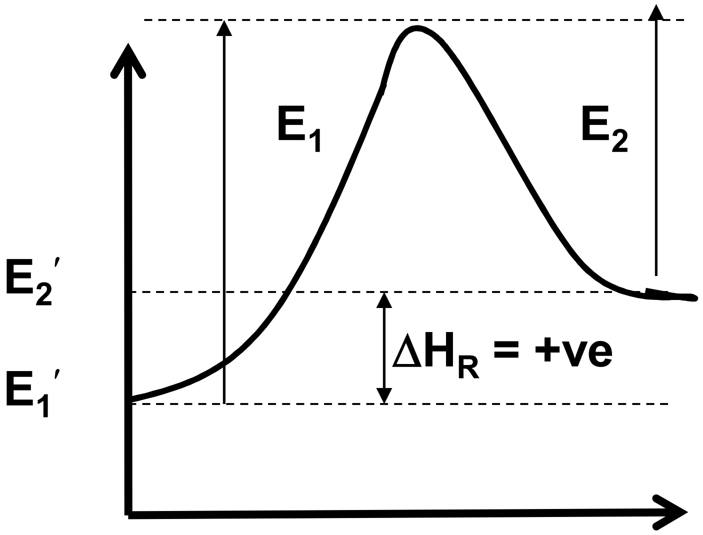


1. Normal behavior – simple reactions
2. Heterogeneous reactions dominated by resistance to diffusion
3. Typical explosions, fuel-air mixtures at ignition temperature
4. Catalytic reactions controlled by rate of adsorption, enzymatic reactions
5. Some reactions complicated by side reactions
6. Oxygen + Nitric Oxide



$\Delta H_R = E_2' - E_1' = E_1 - E_2$

Exothermic Reaction



$\Delta H_R = E_2' - E_1' = E_1 - E_2$

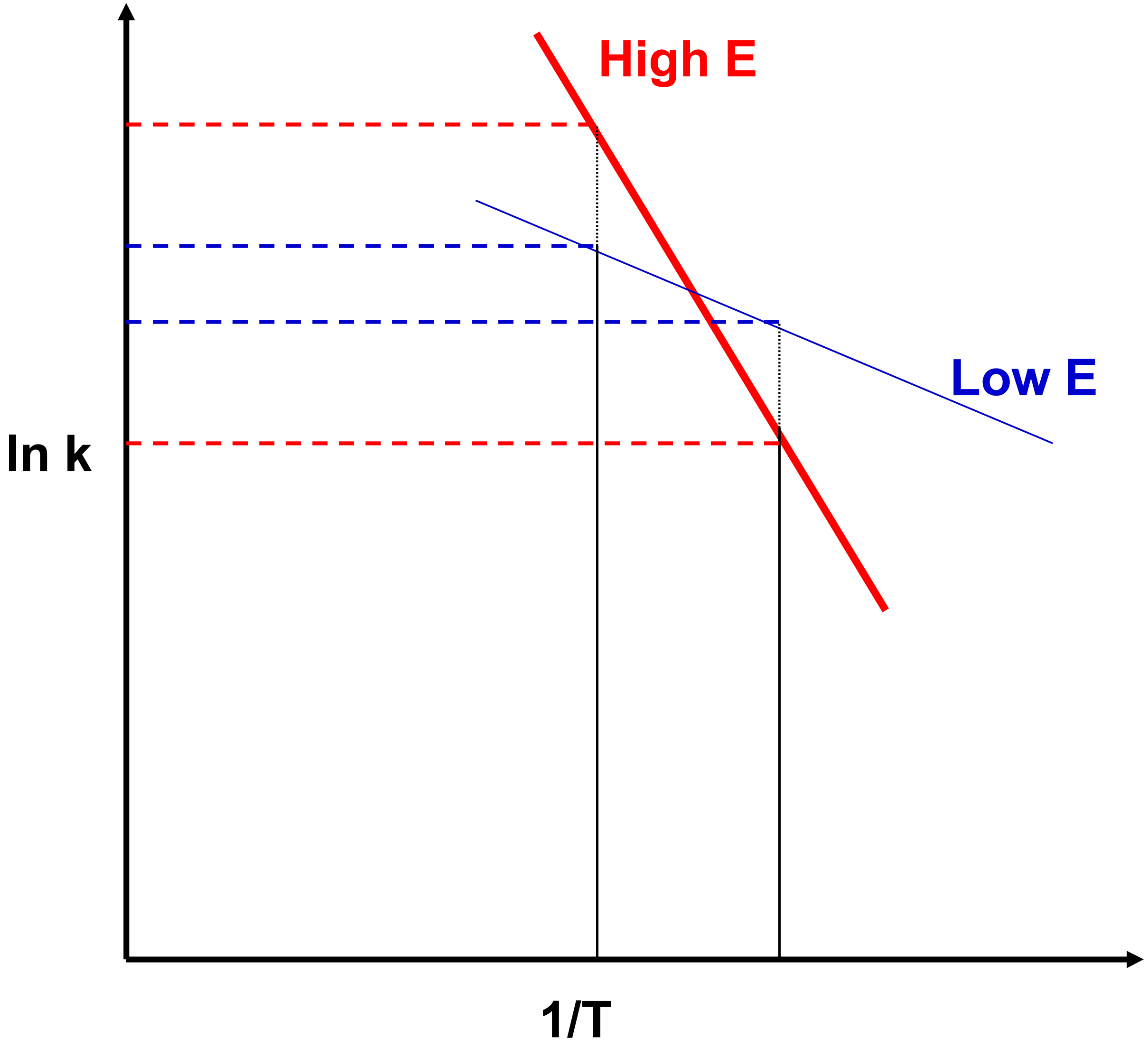
Endothermic Reaction

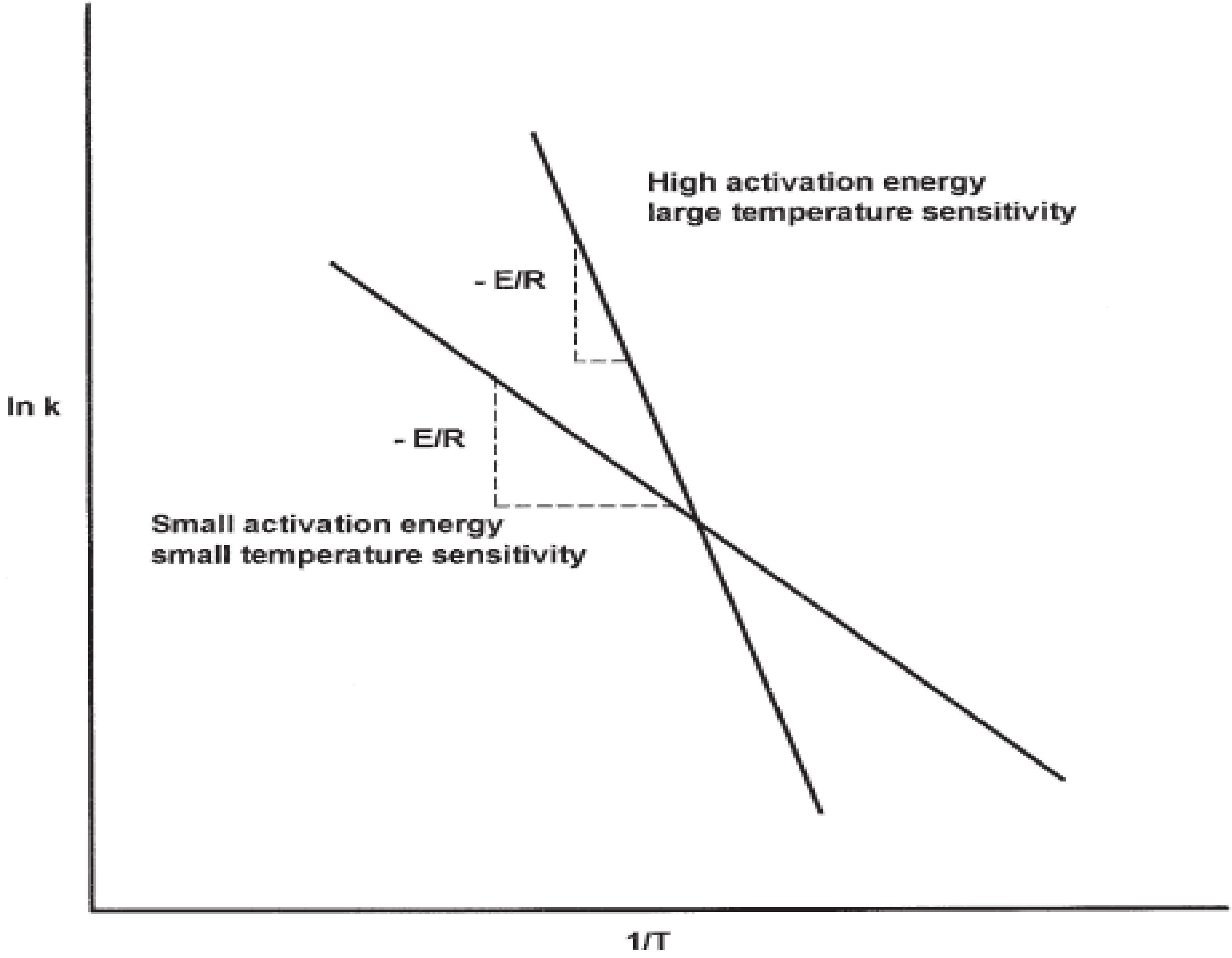
Temperature dependency of Rate

- Effect of temperature on exothermic & endothermic reactions ??
- Which reactions are more temperature sensitive (high E or low E)??
- Effect of temperature on exothermic & endothermic reversible reactions ??

Exothermic reaction: $E_{Forward} < E_{Backward}$
Endothermic reaction: $E_{Forward} > E_{Backward}$

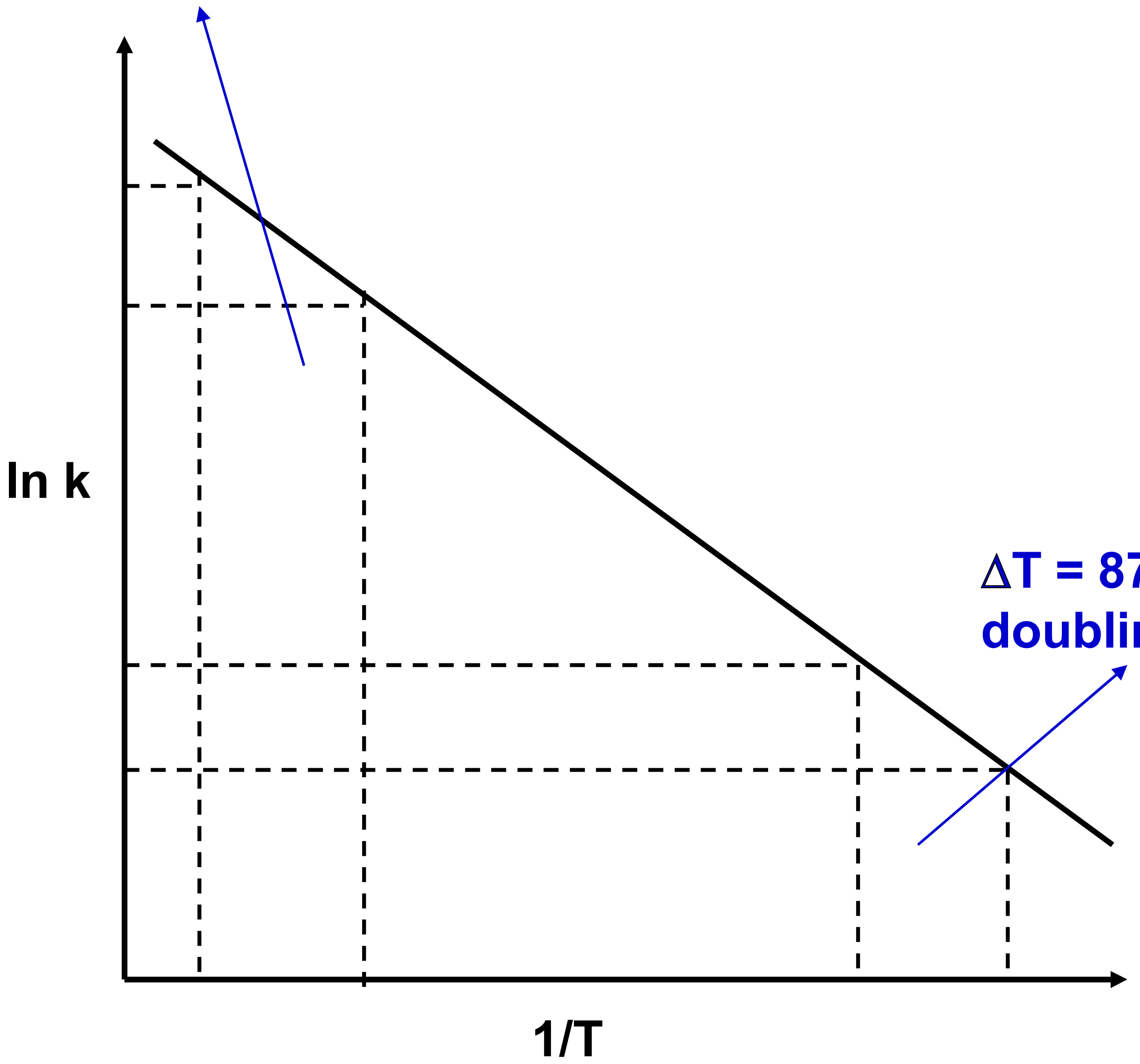
- Are reactions sensitive at low temperature ranges or high temperature ranges ??


High E
Low E
ln k
1/T



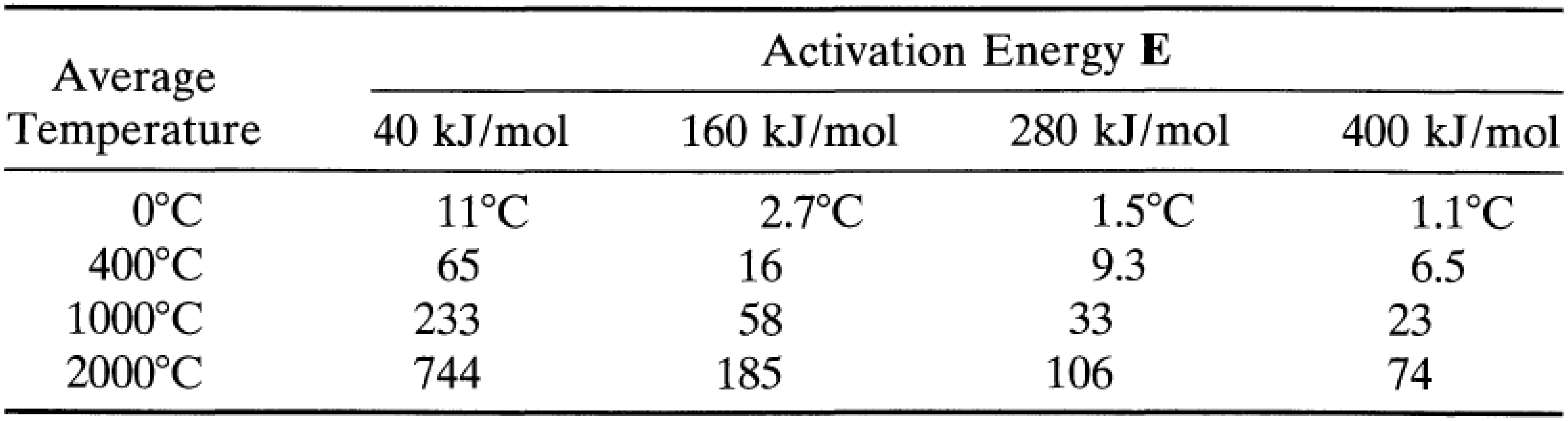
Reaction rate temperature dependence

ΔT = 1000K for doubling the rate



ΔT = 87K for doubling the rate

Temperature Rise Needed to Double the Rate of Reaction for Activation Energies and Average Temperatures



Average Temperature	Activation Energy **E**			
	40 kJ/mol	160 kJ/mol	280 kJ/mol	400 kJ/mol
0°C	11°C	2.7°C	1.5°C	1.1°C
400°C	65	16	9.3	6.5
1000°C	233	58	33	23
2000°C	744	185	106	74

- **Note that reactions are more sensitive at low temperature**
- **Reactions with higher E are more sensitive to temperature**

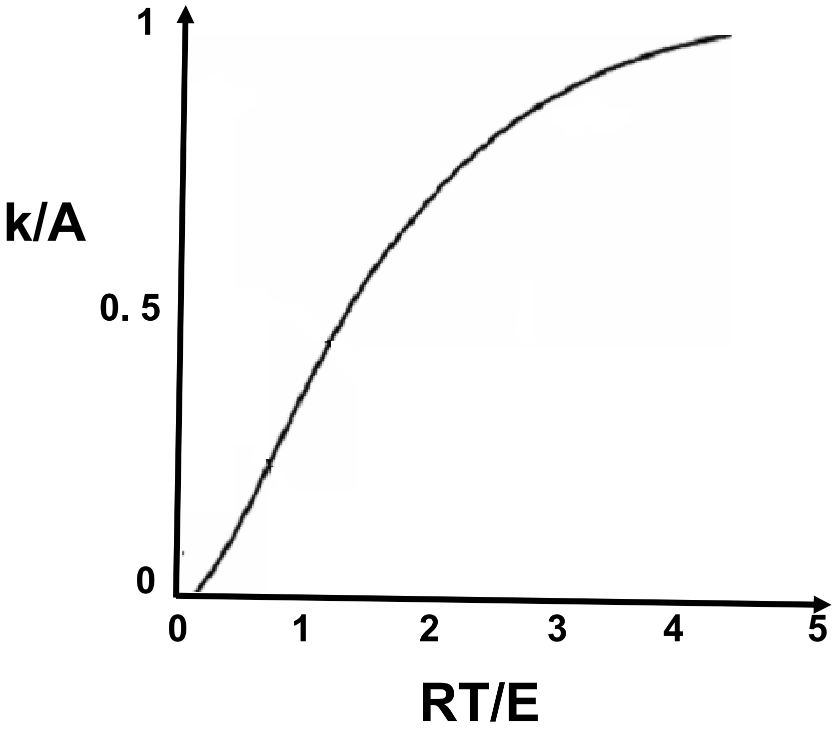
Temperature dependency of Rate

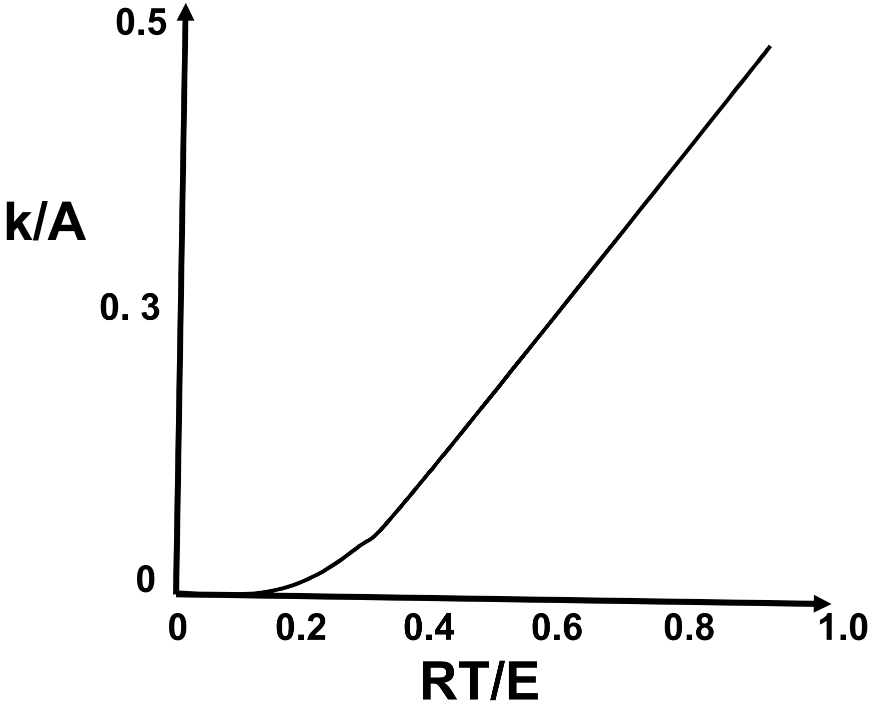
1. Arrhenius' law: $k = A\, e^{(-E/RT)}$

2. Collision Theory: $k \propto T^{1/2}\, e^{(-E/RT)}$

3. Transition State Theory: $k \propto T e^{(-E/RT)}$

$$k = k_0 T^n\, e^{(-E/RT)}$$





- In industrial practice E/R ranges from 5000 to 35000
- Therefore RT/E < 0.6 is of practical interest
- k approaches A at extreme temperatures
- In practice k is several orders of magnitude lower to A