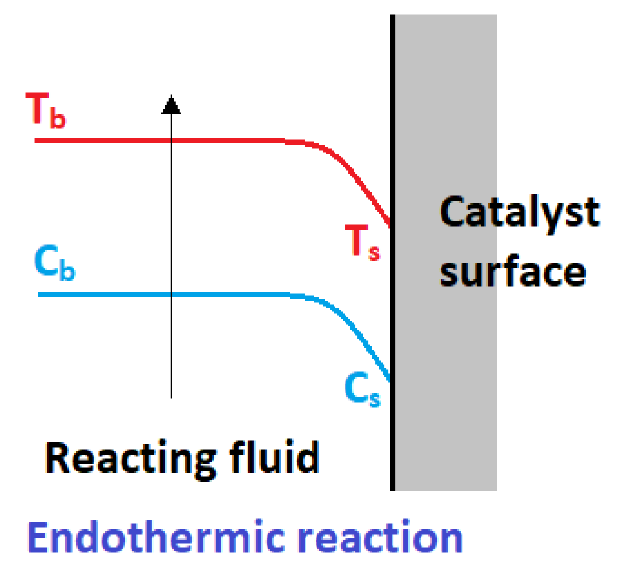
# External Transport Processes in Heterogenous Reactions

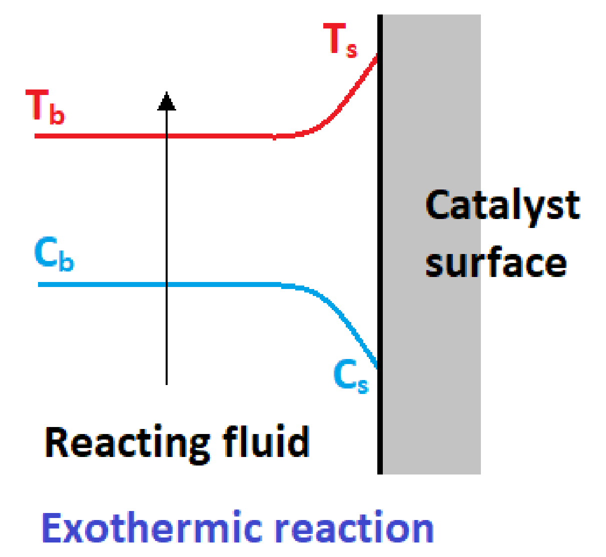
Book: *Chemical Engineering Kinetics*, J. M. Smith, 3rd Edition (Chapter 10), 2nd Edition (Chapter 10)
*Elements of Chemical Reaction Engineering*, H.S. Fogler, 4th Edition (Chapter 11)

- No matter how active a catalyst particle is, it can be effective only if the reactants can reach the catalyst surface
- The transfer of reactant from the bulk to the catalyst surface requires the concentration driving force
- Whether the difference in concentration between the bulk fluid and particle surface is significant or not depends on the mass transfer coefficient between the fluid and surface (velocity pattern in the fluid near the surface, physical properties of the fluid) and the rate constant for catalytic reaction
- As the concentration of the reactant is less at the catalyst surface than at the bulk fluid ($C_s < C_b$), the *observed global rate* is less than the *intrinsic rate* evaluated at the concentration of the reactant in the *bulk* fluid

- Similar to the concentration gradient, there is a temperature gradient between the bulk and surface
- For *endothermic reactions*, catalyst surface temperature is lower than that of the bulk ($T_s < T_b$), the observed rate is lower than that calculated at the bulk temperature



- For *exothermic reactions*, the surface temperature is higher than the bulk fluid conditions ($T_s > T_b$). Whether the *global rate will be lower or higher* than bulk conditions, will depend on the conditions, as high temperature increases the rate while drop in reactant concentration reduces the rate.



- In this chapter, the objective is to study how the external processes affect the global rate which will then be required to design heterogenous reactors
- The external transport processes (heat and mass transfer) which influence the global rate are in series with the chemical reaction occurring on or in the catalyst
- Mass and heat transfer coefficients between fluid and catalyst depends on the flow and geometric arrangement of fluid and catalyst particles/pellets, i.e., type of reactor
- Thus, coefficients are different in a fixed bed arrangement (fluid flows around stationary particles) and in a fluidized bed arrangement (both fluid and particles are in motion)

- For a non-porous catalyst pellet undergoing a reaction of the $nth$ order, the rate can be expressed as

$$r_p = k_m a_m (C_b - C_s)$$

$k_m$ : mass transfer coefficient between bulk gas and solid,

$a_m$: external surface area per unit mass of catalyst

$$r_p = kC_s^n$$

Equating the two rate expressions we have, $k_m a_m (C_b - C_s) = kC_s^n$

- This can be written as, $\boxed{k_m a_m (C_b - C_s) = kC_s}$ for a first order reaction

$$C_s = \frac{k_m a_m}{k_m a_m + k} C_b$$

$$\boxed{r_p = k_o C_b = \frac{1}{\frac{1}{k} + \frac{1}{k_m a_m}} C_b}$$

where $\boxed{\frac{1}{k_o} = \frac{1}{k} + \frac{1}{k_m a_m}}$

## Case 1

- If the reaction rate constant is much larger than mass transfer coefficient ($k \gg k_m a_m$), the surface concentration ($C_s$) approaches zero
- The rate ($k_o$) depends on the rate of transfer of reactant to the surface, which reacts as soon as it reaches it. Thus, the reaction is controlled by the mass transfer term and is known as the *diffusion control regime*

$$\boxed{r_p = k_m a_m C_b}$$

- Here, kinetics is not important. The reaction will appear to follow first order kinetics regardless of the functional form of the intrinsic rate expression
- The activation energy for such reactions will correspond to the activation energy of $k_m$ which is usually 4 -12 kJ/mol
- The importance of considering external diffusion effects can be seen from the following situation –
  - Suppose a second order reaction is carried out in a diffusion control regime
  - The rate would be, $r_p = k_m a_m C_b$
  - Experimental rate data ($r_p$) plotted versus $C_b$ would yield a straight line
  - If diffusion is not considered and the general expression, $kC_s^n$ is used to interpret the data, the order $n$ will be identified as = 1
  - This is a wrong conclusion since the equation is actually second order

**Case 2**

- If the reaction rate is much slower than mass transfer ($k \ll k_m a_m$), then surface concentration ($C_s$) approaches the bulk concentration ($C_b$)
- The rate is given by $r_p = kC_s^n$

**Case 3**

- When resistances due to diffusion and reaction are both significant

$$r_p = k_o C_b = \frac{1}{\frac{1}{k} + \frac{1}{k_m a_m}} C_b$$

- If $k$ and $k_m$ are known, the global rate ($r_p$) can be calculated in terms of $C_b$
- Alternately, if global rate ($r_p$) and hence $k_o$ is known, intrinsic rate constant, $k$ can be calculated if $k_m$ is known

- For **non first order reactions**, it is not easy to eliminate $C_s$
- In such cases, knowing $r_p$ and $k_m$, $C_s$ is calculated from $r_p = k_m a_m (C_b - C_s)$
- This value is then used in $r_p = kC_s^n$ to evaluate $k$ and $n$

# Overall effectiveness factor ($\eta_{ov}$)

- If the solid catalyst is porous with internal diffusional limitations,

$$r_p = \eta r_s(C_s, T_s) = \eta k C_s^n$$

and $r_p = k_m a_m (C_b - C_s)$

- Since the bulk concentration term ($C_b$) is usually known and $C_b$ is different from $C_s$ due to external mass transfer, a new term known as **overall effectiveness factor ($\eta_{ov}$)** is defined
- This term considers all the resistances present

$$\boxed{r_p = \eta r_s(C_s, T_s) = \eta_{ov}\, r_s(C_b, T_b)}$$

- For a first order isothermal reaction.

$$r_p = \eta_{ov}\, k_{int}\, C_b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$= \eta k_{int}\, C_s \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$= k_m a_m (C_b - C_s) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$(\eta_{ov}\, k_{int}) = k_{obs}$$

From (2) and (3), $\eta k_{int}\, C_s = k_m a_m (C_b - C_s)$

$$\boxed{C_s = \frac{k_m a_m}{k_m a_m + \eta k_{int}} C_b}$$

Now from (1) and (2), $\eta_{ov}\, k_{int}\, C_b = \eta k_{int}\, C_s$

$$\eta_{ov}\, k_{int}\, C_b = \eta k_{int} \left[\frac{k_m a_m}{k_m a_m + \eta k_{int}} C_b\right]$$

or, $$\boxed{\eta_{ov} = \frac{\eta k_m a_m}{k_m a_m + \eta k_{int}}}$$

or, $$\boxed{\frac{1}{\eta_{ov}} = \frac{1}{\eta} + \frac{k_{int}}{k_m a_m}} \quad \text{......................... (4)}$$

Multiplying by $\frac{1}{k_{int}}$ and replacing $k_{obs} = (\eta_{ov}\, k_{int})$

$$\frac{1}{\eta_{ov} k_{int}} = \frac{1}{\eta k_{int}} + \frac{1}{k_m a_m}$$

$$\boxed{\frac{1}{k_{obs}} = \frac{1}{\eta k_{int}} + \frac{1}{k_m a_m}} \quad \text{......................... (5)}$$

For a spherical catalyst, $a_m = \frac{4\pi R^2}{\frac{4}{3}\pi R^3 \rho_p} = \frac{3}{R\rho_p}$

The term in equation (4) is written as, $\frac{k_{int}}{k_m a_m} = \frac{k_{int}}{k_m} \times \frac{R\rho_p}{3} \times \frac{R}{R} \times \frac{D_e}{D_e} = \frac{R^2}{3} \times \frac{k_{int}\rho_p}{D_e} \times \frac{1}{\frac{k_m R}{D_e}} \times \frac{3}{3}$

$$\boxed{\frac{k_{int}}{k_m a_m} = \frac{3\phi_s^2}{Bi_m}}$$

$Bi_m$: Biot Number for mass transfer

Replacing the value of $\frac{k_{int}}{k_m a_m}$ in equation (4) we have,

$$\boxed{\frac{1}{\eta_{ov}} = \frac{1}{\eta} + \frac{3\phi_s^2}{Bi_m}}$$

where $\boxed{\phi_s = \frac{R}{3}\sqrt{\frac{k_{int}\rho_p}{D_{e.A}}}}$ and $\boxed{Bi_m = \frac{k_m R}{D_e}}$

$$Bi = \frac{hL}{k} = \frac{1/{}^{k}/_{L}}{1/h}$$

$$= \frac{Heat\ transfer\ resistance\ inside\ the\ body}{Heat\ transfer\ resistance\ at\ the\ surface}$$

Values of $Bi_m$ range between 10 – 100

(rate of external mass transfer > intraparticle diffusion)

$$Bi_m = \frac{k_m R}{D_e} = \frac{1/{}^{D_e}/_{R}}{1/k_m}$$

$$= \frac{Internal\ resistance\ to\ mass\ transfer}{Resistance\ to\ mass\ transfer\ at\ the\ surface}$$

For small values of $\phi_s$, the second term → 0

and $\eta_{ov} \approx \eta$

For large values of $k_m$, the value of $Bi_m$ is large, and second term → 0

and $\eta_{ov} \approx \eta$

# False activation energy

- Diffusion effects can lead to a false activation energy
- For a non-porous catalyst and first order reaction, the observed rate (global) can be used to calculate the overall rate constant ($k_o$)

$$\boxed{r_p = k_o C_b = \frac{1}{\frac{1}{k} + \frac{1}{k_m a_m}} C_b}$$

- If external diffusion is neglected, an apparent activation energy $(E')$ can be calculated from

$$\boxed{k_o = A' e^{-E'/RT}}$$

where $A'$ is the apparent frequency factor

- If external diffusion has a significant effect, this would give an erroneous value

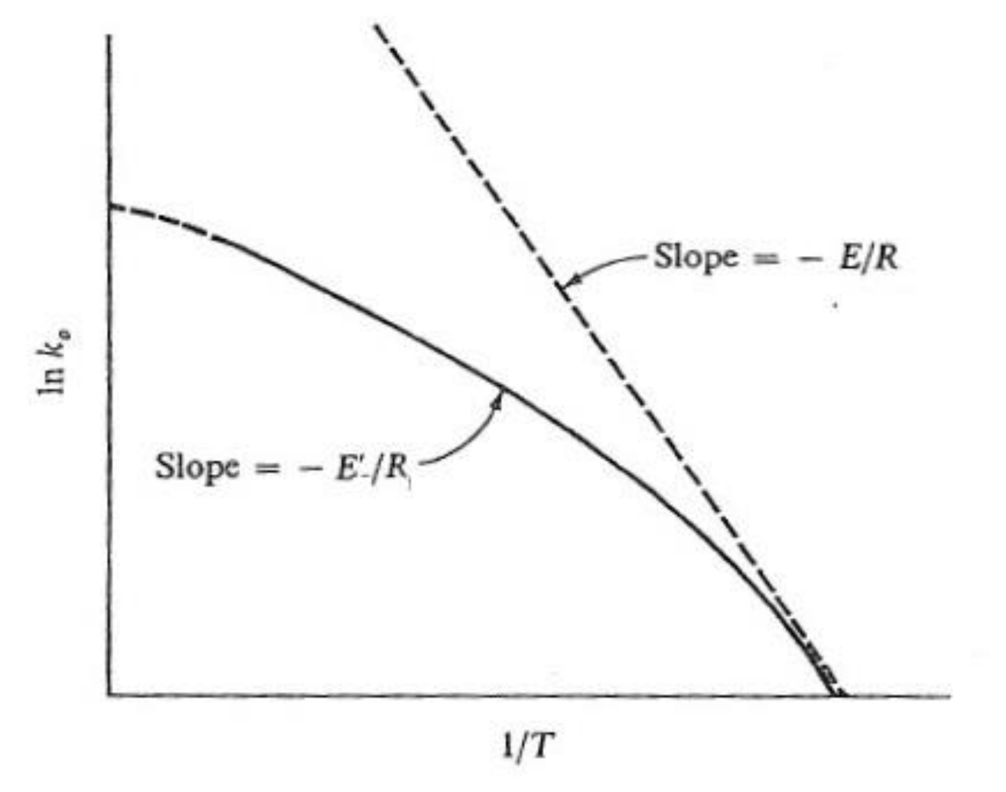
$$\frac{1}{k_o} = \frac{1}{k} + \frac{1}{k_m a_m} = \frac{1}{A e^{-E/RT}} + \frac{1}{k_m a_m}$$

$$\boxed{k_o = \frac{A k_m a_m e^{-E/RT}}{k_m a_m + A e^{-E/RT}}}$$

$$k_o = \frac{A k_m a_m e^{-E/_{RT}}}{k_m a_m + A e^{-E/_{RT}}}$$

- At low temperatures (high values of 1/T), the slope of the straight line gives the correct activation energy
- At **low temperature,** $\boldsymbol{k_o \approx A e^{-E/_{RT}}}$

- As temperature increases (lower values of 1/T), the line curves and ultimately flattens out to a nearly horizontal line
- At **high temperature,** $\boldsymbol{k_o \approx k_m a_m}$
- The almost flattening of the curve is because $k_m$ is nearly independent of temperature or is relatively insensitive to temperature



- When <u>experimental rate data shows a curved line for the ln k versus 1/T plot</u> (as in the figure), <u>it is possible that external diffusional resistances are important</u>

# Mass transfer coefficient

The most convenient form for correlating mass transfer coefficient is the Chilton-Colburn $j_D$ factor

$$\boxed{j_D = \frac{k_m \rho}{G}\left(\frac{\mu}{\rho D}\right)^{2/3}}$$

For mass transfer, $\boxed{Sh = f(Re.Sc)}$

$Sherwood\ Number, Sh = \frac{k_m \rho}{G}$ $Reynolds\ Number, Re = \frac{d_p G}{\mu}$ $Schmidt\ Number, Sc = \frac{\mu}{\rho D}$

$G$ = superficial mass velocity

$d_p$ = equivalent dimeter of catalyst pellet

$D$= molecular diffusion coefficient of the species being transferred

$\mu$ = fluid viscosity

$\rho$ = fluid density

$k_m$ = mass transfer coefficient

$j_D$ factor can be estimated from the following correlation

$$\boxed{j_D = \frac{0.458}{\varepsilon_B}\left(\frac{d_p G}{\mu}\right)^{-0.407}}$$

$3 < \frac{d_p G}{\mu} < 2000$

$\varepsilon_B$= bed porosity

- Another correlation for estimating $j_D$ factor

$$\boxed{j_D = 1.24\left(\frac{Re}{1-\varepsilon_B}\right)^{-0.39}}$$

for $50 < Re = \frac{d_p G}{\mu} < 500$ valid for both liquids and gases

for $0.6 < Sc < 2000$

$\varepsilon_B$ = bed porosity and $0.3 < \varepsilon_B < 0.5$

- Mass transfer for <u>flow around a single sphere</u>

$$\boxed{Sh = \frac{k_m d_p}{D_{AB}} = 2 + 0.6Sc^{1/3}Re^{1/2}}$$

This is called the ***Froessling equation***

# External temperature gradient

- For any single reaction, it is possible to relate $(T_b - T_s)$ and $(C_b - C_s)$
- At steady state, the heat generated in pellet due to reaction will be equal to the heat transferred to the surroundings

Thus,

$$\boxed{r_p(-\Delta H_R) = ha_m(T_s - T_b)}$$

and

$$\boxed{k_m a_m(C_b - C_s)(-\Delta H_R) = ha_m(T_s - T_b)}$$

Simplifying,

$$\boxed{(T_s - T_b) = (-\Delta H_R)\frac{k_m}{h}(C_b - C_s)}$$

- The correlation for heat transfer is related by

$$\boxed{j_H = \frac{h}{C_p G}\left(\frac{C_p \mu}{k_f}\right)^{2/3}}$$

$k_f$ is the thermal conductivity of the fluid

$$j_H = \frac{h}{C_p G}\left(\frac{C_p \mu}{k_f}\right)^{2/3} = \frac{h}{C_p G}(Pr)^{2/3}$$

Or,

$$\boxed{h = j_H \frac{G C_p}{(Pr)^{2/3}}}$$

From the mass transfer correlation

$$\boxed{j_D = \frac{k_m \rho}{G}\left(\frac{\mu}{\rho D}\right)^{2/3}}$$

Or,

$$\boxed{k_m = j_D \frac{G}{\rho (Sc)^{2/3}}}$$

Replacing the values of $h$ and $k_m$ in the expression to estimate $(T_s - T_b)$, we have,

$$(T_s - T_b) = (-\Delta H_R) \times \frac{j_D G}{\rho (Sc)^{2/3}} \times \frac{(Pr)^{2/3}}{j_H G C_p} \times (C_b - C_s)$$

For many gases, $j_D \approx j_H$ and $\frac{Sc}{Pr} = Lewis\ Number \approx 1$

$$(T_s - T_b) = (-\Delta H_R) \times \frac{j_D G}{\rho (Sc)^{2/3}} \times \frac{(Pr)^{2/3}}{j_H G C_p} \times (C_b - C_s)$$

$$\boxed{(T_s - T_b) \approx \frac{(-\Delta H_R)}{\rho C_p}(C_b - C_s)}$$

- Due to the first term in the right hand side of the equation, $(T_s - T_b)$ may be appreciable even when $(C_b - C_s)$ is small
- <u>Hence, external heat transfer can have an effect on the global rate even when external mass transfer is negligible</u>
- However, when intra pellet heat transfer is small, external mass transfer is small
- When external mass transfer controls the global rate (i.e., $C_s \rightarrow 0$), the **maximum temperature rise** would be that corresponding to adiabatic temperature rise $\left[\frac{(-\Delta H_R)}{\rho C_p}\right]$ for the reaction

$$\boxed{(T_s - T_b)_{max} \approx \frac{(-\Delta H_R)}{\rho C_p}(C_b)}$$

# Mears criterion for external diffusion

- Mears criterion uses the measured rate of reaction, $r_p$ to determine if mass transfer from the bulk gas phase to the catalyst surface can be neglected

$$\boxed{\frac{r_p \rho_b R n}{k_m C_b} < 0.15}$$

$n$ = reaction order     $R$ = catalyst particle radius     $\rho_b$ = bulk density of catalyst bed

$k_m$= mass transfer coefficient     $C_b$ = reactant concentration in bulk phase

- When the above criterion is satisfied, external mass transfer can be neglected
- Mears also proposed that bulk fluid temperature, $T_b$ would be equal to the external surface temperature $T_s$ when

$$\boxed{\left|\frac{(-\Delta H_R) r_p \rho_b R E}{h T_b^2 R_g}\right| < 0.15}$$

$(-\Delta H_R)$ = heat of reaction     $E$= activation energy     $R_g$ = gas constant

$h$ = heat transfer coefficient between gas and pellet

# Effect of external transport processes on selectivity

- For **parallel independent reactions** (isothermal)

$A \xrightarrow{k_1} B$ (desired) [First order reactions]

$R \xrightarrow{k_2} S$

With external resistance, selectivity, $S_P = \frac{r_B}{r_S} = \frac{k_{1o} C_{As}}{k_{2o} C_{Rs}}$

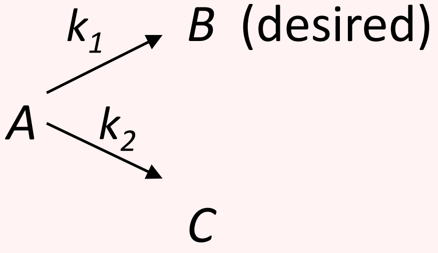
$$\frac{r_B}{r_S} = \frac{C_{Ab}}{\left[\frac{1}{k_1} + \left(\frac{1}{k_m a_m}\right)_A\right]} \times \frac{\left[\frac{1}{k_2} + \left(\frac{1}{k_m a_m}\right)_R\right]}{C_{Rb}}$$

- With no external resistances, selectivity, $S'_P = \frac{r_B}{r_S} = \frac{k_1 C_{Ab}}{k_2 C_{Rb}}$

$$\boxed{\frac{S_P}{S'_P} = \frac{\frac{(k_m a_m)_R + k_2}{k_2 (k_m a_m)_R}}{\frac{(k_m a_m)_A + k_1}{k_1 (k_m a_m)_A}} \times \frac{k_2}{k_1} = \frac{\frac{(k_m a_m)_R + k_2}{(k_m a_m)_R}}{\frac{(k_m a_m)_A + k_1}{(k_m a_m)_A}}}$$

- Since the two mass transfer coefficients are nearly the same for most reaction systems, <u>selectivity is reduced if $k_1 > k_2$</u>

- For **parallel reactions** (isothermal),



Selectivity, $S_P = \frac{r_B}{r_C} = \frac{k_1 C_{As}}{k_2 C_{As}} = \frac{k_1}{k_2}$

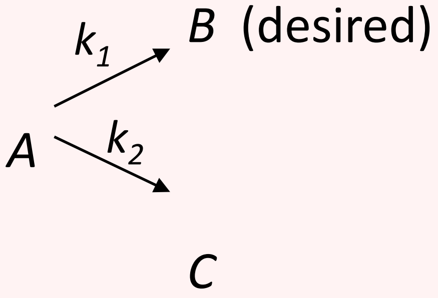
- Selectivity is unaffected no matter how much the surface concentration is reduced due to external diffusional resistance. For such reactions, external diffusional resistance reduces the rate of reaction but not selectivity

- For **series or consecutive reactions**,

$$A \rightleftharpoons B\ (desired) \rightleftharpoons C$$

- The effect of external mass transfer will be to reduce the surface concentration of $A$ below the bulk value
- This reduces the rate of formation of $B$ by the first reaction
- Conversely, the concentration of $B$ will be greater at the catalyst surface (as the mass transfer resistance will reduce the rate at which $B$ is diffused from the surface) than in the bulk fluid
- This increases the rate of disappearance of $B$ by the second reaction
- From qualitative reasoning, we expect that the selectivity of $B$ with respect to $C$ will be reduced by external mass transfer

- **Non-isothermal conditions**
- For **parallel reactions** having the same reaction order,



$$\boxed{\text{Selectivity, } S_P = \frac{r_B}{r_C} = \frac{k_1 C_{As}}{k_2 C_{As}} = \frac{k_1}{k_2} = \frac{A_1 e^{-E_1/RT}}{A_2 e^{-E_2/RT}}}$$

- If $T_s = T_b$, selectivity is more if $E_1 > E_2$
- <u>Selectivity is increased by mass transfer resistances for an exothermic reaction</u> $(T_s > T_b)$ when $E_1$ for the desired reaction is larger than $E_2$ for the undesired reaction, as shown below

$$\frac{(S_p)_{T_s}}{(S_p)_{T_b}} = \frac{\dfrac{A_1 e^{-E_1/RT_s}}{A_2 e^{-E_2/RT_s}}}{\dfrac{A_1 e^{-E_1/RT_b}}{A_2 e^{-E_2/RT_b}}} = \frac{e^{-E_1/RT_s}}{e^{-E_2/RT_s}} \times \frac{e^{-E_2/RT_b}}{e^{-E_1/RT_b}}$$

$$\boxed{\frac{(S_p)_{T_s}}{(S_p)_{T_b}} = \frac{exp\left[\frac{E_1}{R}\left(\frac{1}{T_b} - \frac{1}{T_s}\right)\right]}{exp\left[\frac{E_2}{R}\left(\frac{1}{T_b} - \frac{1}{T_s}\right)\right]} = \frac{exp\left[\frac{E_1}{R}\left(\frac{T_s - T_b}{T_b T_s}\right)\right]}{exp\left[\frac{E_2}{R}\left(\frac{T_s - T_b}{T_b T_s}\right)\right]}}$$

- For exothermic reaction, $T_s > T_b$ and $T_s - T_b$ is positive

  If $E_1 > E_2$, the selectivity at $T_s$ is greater than at $T_b$

- For endothermic reaction, $T_s < T_b$ and $T_s - T_b$ is negative

  If $E_1 > E_2$ , the selectivity at $T_s$ is lower than at $T_b$

- For For **series or consecutive reactions**,

$$A \overset{k_1}{\rightarrow} B\ (desired) \overset{k_2}{\rightarrow} D$$

- If both mass and heat transfer resistance is important, selectivity is reduced by mass transfer resistance and increased by heat transfer resistance provided the reaction is exothermic and $E_1 > E_2$
- The temperature effect is the dominating factor for moderate or high heats of reaction, and selectivity increases