Internal Transport Processes – Reaction and Diffusion in Porous Catalysts

Effect of intrapellet diffusion on measured rates

- In some situations, neglecting the intrapellet diffusion may often lead to circumstances where the measured reaction order and activation energy are not the true values

- This is known as *falsified kinetics*

- Using the definition of effectiveness factor η, the actual rate for a nth order reaction is written as,

$$r_p = \eta k_n C_{As}^n$$

- For large values of Thiele modulus (ϕ) it can be shown that

$$\eta = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{R} \sqrt{\frac{D_e}{k_n \rho_p C_{As}^{n-1}}}$$

- Therefore, in severely pore-diffusion limited region (large ϕ), we have

$$r_p = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{R} \sqrt{\frac{D_e}{k_n \rho_p C_{As}^{n-1}}} \times k_n C_{As}^n$$

$$r_p = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{R} \sqrt{\frac{D_e k_n}{\rho_p}} \; C_{As}^{(n+1)/2}$$

- Experiments are carried out to obtain reaction rate data for such a catalyst in order to determine the order and rate constant

- The data is correlated by power law kinetics to obtain the measured (observed) rate constant k_{obs} and the measured reactor order, m. Then,

$$r_p = k_{obs} C_{As}^m$$

- Comparing this equation with the rate expression obtained earlier, $r_p = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{R} \sqrt{\frac{D_e k_n}{\rho_p}} \ C_{As}^{(n+1)/2}$, it is seen that **in a region of strong pore diffusional limitations**,

    (i) Measured reaction order, $\boxed{m = \frac{n+1}{2}}$

    For a *first order reaction*, there is *no difference* between the *observed order and the actual order*

    For a *second order reaction*, $n = 2$, but $m = \frac{2+1}{2} = 1.5$. Therefore, *observed order is 1.5* but the *actual order is 2*

    (ii) The experimentally measured rate constant is $\boxed{k_{obs} = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{R} \sqrt{\frac{D_e k_n}{\rho_p}}}$

    In a *severely pore-diffusion limited* regime, k_{obs} *is inversely proportional to R*

    If there is *no diffusional resistance*, then k_{obs} *is independent of R*

(iii) Although D_e varies as $T^{3/2}$, for small temperature ranges D_e can be represented by an *Arrhenius type equation* with activation energy of diffusion given by E_{diff}

If the measured activation energy is E_{obs}, and the intrinsic activation energy is E_{int}, then from the two expressions of rate, $r_p = k_{obs} C_{As}^m$ and $r_p = \left(\dfrac{2}{n+1}\right)^{1/2} \dfrac{3}{R} \sqrt{\dfrac{D_e k_n}{\rho_p}}\, C_{As}^{(n+1)/2}$

$$\boxed{exp\left[-\dfrac{E_{obs}}{RT}\right] = exp\left[-\dfrac{E_{int}+ E_{diff}}{2RT}\right]}$$

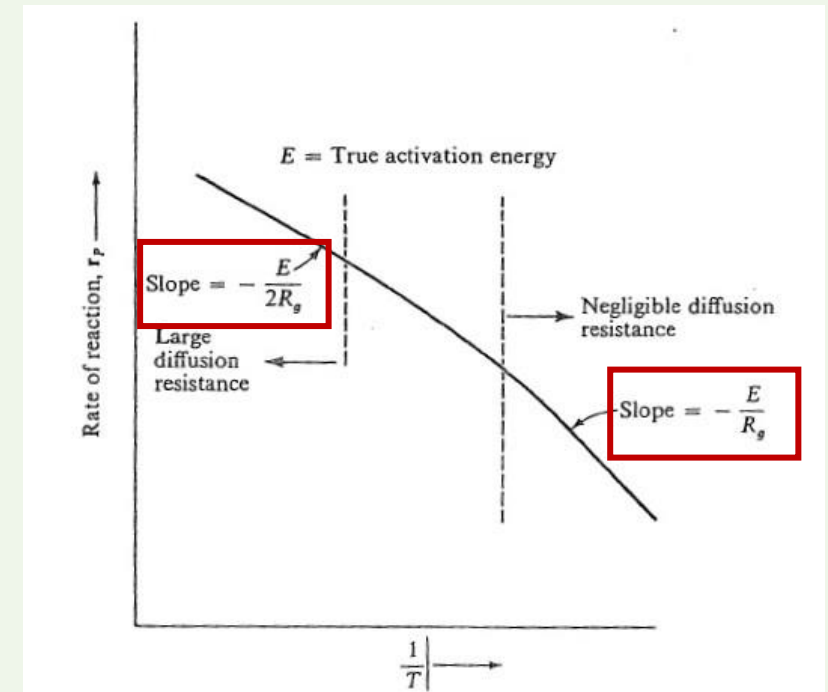Therefore, $\boxed{E_{obs} = \dfrac{E_{int}+ E_{diff}}{2}}$

If $E_{diff} \approx 0$, $\boxed{E_{obs} = \dfrac{E_{int}}{2}}$

$$k_{obs} = k_{obs,o}\, exp\left(-\dfrac{E_{obs}}{RT}\right)$$

$$k_n = k_{n,o}\, exp\left(-\dfrac{E_{int}}{RT}\right)$$

$$D_e = D_{e,o}\, exp\left(-\dfrac{E_{diff}}{RT}\right)$$

- If k_{obs} is measured at different temperatures and the **k_{obs} is plotted versus 1/T**, the Arrhenius plot generated is shown here

- At **low temperature**, intrinsic rate constant is low, resulting in low ϕ and diffusional resistances are not present
  Observed activation energy (E_{obs}) = True activation energy (E_{int})

- At **high temperatures**, ϕ is high and
  Observed activation energy (E_{obs}) = $\dfrac{\text{True activation energy}}{2}$ ($\dfrac{E_{int}}{2}$)

- **When diffusional resistances affect rate of reaction, then E_{obs} varies with temperature**

E = True activation energy
Slope = $-\dfrac{E}{2R_g}$
Large diffusion resistance
Negligible diffusion resistance
Slope = $-\dfrac{E}{R_g}$
Rate of reaction, r_p
$\dfrac{1}{T}$

Measurement of effectiveness factor (η)

Case I

If D_e is known, and k_{obs} is experimentally obtained

For a first order reaction, $\eta = \dfrac{k_{obs} C_{As}}{k_{int} C_{As}} = \dfrac{k_{obs}}{k_{int}}$

- A value of η is assumed
- ϕ_s is calculated from the graph or an equation for this value of η
- Using this value of ϕ_s, k_{int} is calculated from $\quad k_{int} = \dfrac{9\phi_s^2 D_e}{R^2 \rho_p}$
- Compare k_{obs} with (ηk_{int})
- Iterate by choosing different values of η till k_{obs} becomes equal to ηk_{int}

Case II

If D_e is not known, and reaction rates for different pellet sizes under identical experimental conditions are obtained (same C_s , D_e independent of size)

Now, $\boxed{r_p = \eta k C_{As}}$

- Ratio of the rates for two particle sizes 1 and 2 are $\boxed{\dfrac{(r_p)_2}{(r_p)_1} = \dfrac{\eta_2}{\eta_1}}$

- From the expression for ϕ_s we can say, $\boxed{\dfrac{(\phi_s)_2}{(\phi_s)_1} = \dfrac{R_2}{R_1}}$

- We also know that $\boxed{\eta_1 = \dfrac{1}{(\phi_s)_1}\left[\dfrac{1}{tanh3(\phi_s)_1} - \dfrac{1}{3(\phi_s)_1}\right]}$

- and $\boxed{\eta_2 = \dfrac{1}{(\phi_s)_2}\left[\dfrac{1}{tanh3(\phi_s)_2} - \dfrac{1}{3(\phi_s)_2}\right]}$

- These four equations than can be solved simultaneously to find the four unknowns - $\eta_1, \eta_2, (\phi_s)_1$ and $(\phi_s)_2$

The method used for Case II fails if ϕ_s is very large ($\phi_s = \frac{1}{\eta}$)

- If R_1 or R_2 is very small (eg., powder), ϕ_s is small and $\eta \to 1$

    Therefore,

$$\frac{\eta_2}{\eta_1} = \frac{(r_p)_2}{(r_p)_1}$$

$$\frac{(r_p)_2}{(r_p)_1} = \frac{\eta_2 f(C_s)}{1 \cdot f(C_s)} = \frac{\eta_2 f(C_s)}{f(C_s)}$$

$$\boxed{\eta_2 = \frac{(r_p)_2}{(r_p)_1}}$$

Example

The first order reaction $A \rightarrow B$ was carried out over two different sized pellets. The reactor was operated such that external mass transfer resistance was negligible. The results of two experimental runs are given below:

	Measured rate (r_p) (mol/g cat.s) x 10^5	Pellet radius (R) (m)
Run 1	3	0.01
Run 2	15	0.001

(a) Estimate the Thiele modulus and effectiveness factor for each pellet

(b) How small should the pellet be made to virtually eliminate all internal diffusional resistances?

(a) $\quad \dfrac{(r_p)_2}{(r_p)_1} = \dfrac{\eta_2}{\eta_1} = \dfrac{15}{3} = 5 \quad \Rightarrow \quad \eta_2 = 5\eta_1$

$\quad \dfrac{(\phi_s)_2}{(\phi_s)_1} = \dfrac{R_2}{R_1} = \dfrac{0.001}{0.01} = 0.1 \quad \Rightarrow \quad (\phi_s)_2 = 0.1(\phi_s)_1$

Since, $\eta = \dfrac{1}{\phi_s}\left[\dfrac{1}{tanh3\phi_s} - \dfrac{1}{3\phi_s}\right]$

$$\dfrac{\eta_1}{\eta_2} = \dfrac{\dfrac{1}{(\phi_s)_1}\left[\dfrac{1}{tanh3(\phi_s)_1} - \dfrac{1}{3(\phi_s)_1}\right]}{\dfrac{1}{(\phi_s)_2}\left[\dfrac{1}{tanh3(\phi_s)_2} - \dfrac{1}{3(\phi_s)_2}\right]} = \dfrac{3}{15}$$

$\therefore$ $\dfrac{\left[\dfrac{1}{tanh3(\phi_s)_1} - \dfrac{1}{3(\phi_s)_1}\right]}{\left[\dfrac{1}{tanh\{3\times0.1(\phi_s)_1\}} - \dfrac{1}{\{3\times0.1(\phi_s)_1\}}\right]} = \dfrac{3}{15} \times \dfrac{(\phi_s)_1}{(\phi_s)_2} = \dfrac{3}{15} \times 10 = 2$

$(\phi_s)_1$	LHS
1	6.756
2	4.265
10	1.4
5	2.13
7	1.719
5.5	1.996 ~ 2

We find that, $(\phi_s)_1$ = **5.5** and $(\phi_s)_2$ = **0.55**

Replacing these values in the relationship between η and ϕ_s,

we get, η_1 = **0.1708** and η_2 = **0.856**

(b) For no diffusional resistance, η can be considered to be equal to 0.95

When $\eta = 0.95$, $0.95 = \dfrac{1}{\phi_s}\left[\dfrac{1}{tanh3\phi_s} - \dfrac{1}{3\phi_s}\right]$

and ϕ_s becomes = 0.3

We know, $\dfrac{(\phi_s)_2}{(\phi_s)_1} = \dfrac{R_2}{R_1}$

Therefore, $R_2 = \dfrac{(\phi_s)_2}{(\phi_s)_1} \times R_1$

$\boldsymbol{R_2} = \dfrac{0.3}{0.55} \times 0.001 = \boldsymbol{5.454 \times 10^{-4}}\ \textbf{m}$

Thus, particles of radius 0.5454 mm will have no diffusional resistances

Non-isothermal pellet

- All discussions about effectiveness factors till now are valid for isothermal conditions

- When large heat effects are involved in the reaction, the temperature in the catalyst surface T_s can be different from the temperature inside the pellet

- When the **reaction is exothermic**, the temperature inside the pellet is higher than T_s

- This more than compensates for the decrease in the rate (or decrease in the concentration) due to diffusional resistances

- The overall effect results in **effectiveness factors greater than unity ($\boldsymbol{\eta > 1}$)**

- Conversely for an endothermic reaction, the temperature and concentration in pores is lower than the surface and $\eta < 1$

For a reaction $A \rightarrow B$, mass balance on a differential element gives

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 D_{e.A}\frac{dC_A}{dr}\right) = k_n \rho_p C_A^n$$

And energy balance is given by

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 k_e \frac{dT}{dr}\right) = k_n \rho_p C_A^n \left(\Delta H_{R,A}\right)$$

Boundary conditions:

$r = 0$ $\dfrac{dC_A}{dr} = \dfrac{dT}{dr} = 0$

$r = R$ $C_A = C_{As},$
$\quad\quad\quad T = T_s$

k_e is the effective thermal diffusivity, varies in the range of 0.1 to 0.7 W/mK

$$k_e = k_s \left(\frac{k_f}{k_s}\right)^{\varepsilon_p}$$

k_s , k_f : thermal conductivity of solid and fluid, ε_p : porosity of pellet

If $D_{e.A}$ and $\Delta H_{R,A}$ are independent of temperature,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 k_e \frac{dT}{dr}\right)\frac{1}{(\Delta H_{R,A})} = \frac{1}{r^2}\frac{d}{dr}\left(r^2 D_{e.A}\frac{dC_A}{dr}\right)$$

Integrating twice we get,

$$T - T_s = \frac{\Delta H_{R,A} D_{e.A}}{k_e}(C_A - C_{As})$$

Though this equation is derived for spherical geometry, the expression has been found to be valid for all geometries and orders

As most catalysts are spoilt at high temperature, it is important to **estimate the maximum temperature rise possible in a catalyst**, $(T_{max} - T_s)$

T_{max} is obtained when $C_A = 0$

Therefore,

$$(T_{max} - T_s) = \frac{(-\Delta H_{R,A})D_{e.A}}{k_e}(C_{As})$$

$$\boxed{\frac{T_{max} - T_s}{T_s} = \beta = \frac{(-\Delta H_{R,A})D_{e.A}}{k_e} \cdot \frac{C_{As}}{T_s}}$$

β: dimensionless temperature rise = *Praeter number*

$$\boxed{\eta_{non-isothermal} = \frac{r_p}{r_s(C_s, T_s)}}$$

$\eta_{non-isothermal}$ depends on ϕ_s, β and γ where

$$\phi_s = \frac{R}{3}\sqrt{\frac{(k)_{T_s}\rho_p}{D_{e.A}}}$$

$$\gamma = \frac{E_{int}}{RT_s} = Arrhenius\ number$$

- The **non-isothermal effectiveness factor** can be estimated from the following plot

- For *endothermic reactions* $(\beta < 0)$, η *is always* < 1

- For *exothermic reactions ($\beta > 0$),* there are **some regions where $\eta > 1$**

- For $\beta > 0.3$ and a narrow range of ϕ, *multiple steady states* **occur**

- This is a situation where there are three values of η for a single value of ϕ

- This is not a common situation though, as very few reactions have $\beta > 0.3$

The **Weisz criterion** is extended to **non-isothermal situations** and the expression for a first order irreversible reaction is
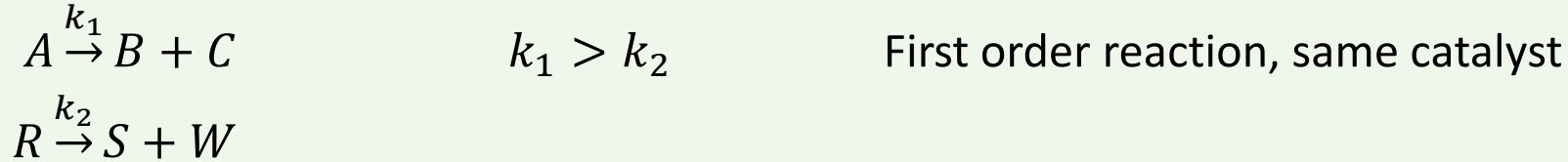
$$\frac{R^2 r_p \rho_p}{C_s\, D_e} e^{\frac{\gamma\beta}{1+\beta}} \leq 1$$

If this is satisfied, intrapellet gradients can be neglected for non-isothermal reactions
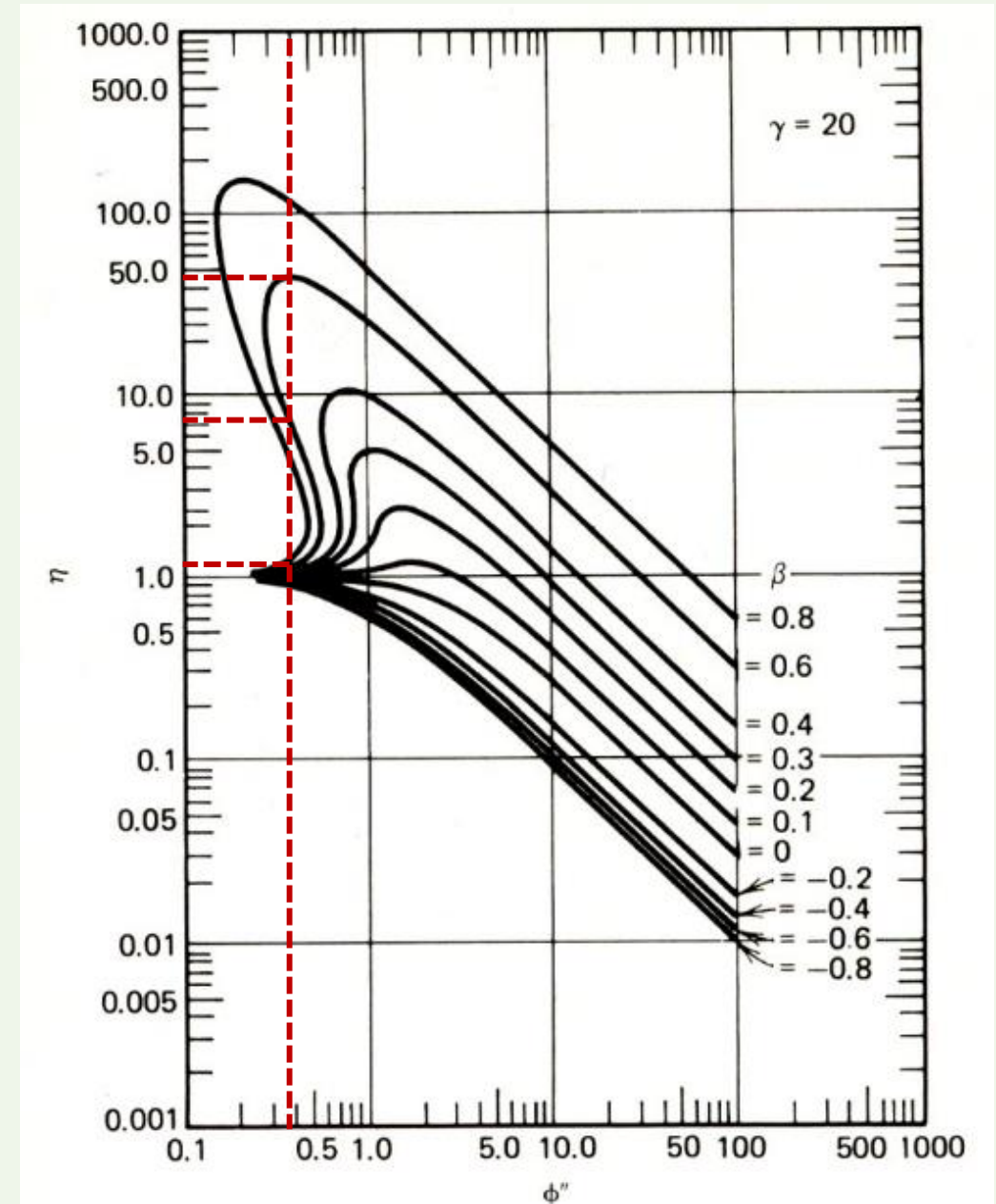
Effect of internal transport resistance on selectivity

- For **parallel independent reactions** (Type I)

$$A \xrightarrow{k_1} B + C \qquad\qquad k_1 > k_2 \qquad\qquad \text{First order reaction, same catalyst}$$

$$R \xrightarrow{k_2} S + W$$

With diffusional limitations, $\dfrac{r_B}{r_S} = \dfrac{\eta_1 k_1 C_{As}}{\eta_2 k_2 C_{Rs}}$

If $\phi_s > 5$ (strong diffusional limitations) $\qquad \eta = \dfrac{1}{\phi_s} \qquad$ and $\qquad \phi_s = \dfrac{R}{3}\sqrt{\dfrac{k\rho_p}{D_e}}$

Selectivity, $\quad S_P = \dfrac{r_B}{r_S} = \dfrac{\dfrac{k_1 C_{As}}{\dfrac{R}{3}\sqrt{\dfrac{k_1 \rho_p}{D_{e,A}}}}}{\dfrac{k_2 C_{Rs}}{\dfrac{R}{3}\sqrt{\dfrac{k_2 \rho_p}{D_{e,R}}}}} = \dfrac{k_1 C_{As}}{k_2 C_{Rs}} \times \dfrac{\dfrac{R}{3}\sqrt{\dfrac{k_2 \rho_p}{D_{e,R}}}}{\dfrac{R}{3}\sqrt{\dfrac{k_1 \rho_p}{D_{e,A}}}}$

If $D_{e,A} \approx D_{e,R}$, $\qquad \boxed{S_P = \dfrac{r_B}{r_S} = \sqrt{\dfrac{k_1}{k_2}}\, \dfrac{C_{As}}{C_{Rs}}}$

Strong intra-pellet diffusional resistance reduces selectivity to the square root of intrinsic rate constants

- For **parallel reactions**,

$$A \underset{k_2}{\overset{k_1}{\swarrow}} \begin{matrix} B \text{ (desired)} \\ S \end{matrix}$$
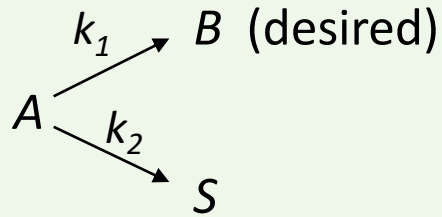
- If both reactions are first order and irreversible, *selectivity is not affected by internal mass transport*. The ratio of the rates is k_1/k_2 at any position in the pellet

- If the **kinetics of the two reactions are different, diffusion has an effect on selectivity**

- If reaction 1 is first order ($r_{p1} = k_1 C_{As}$) and reaction 2 is second order in A ($r_{p2} = k_2 C_{As}^2$), the reduction in the concentration of A due to diffusion resistance would lower the rate of reaction 2 more than that of reaction 1. For this, **the *selectivity of B would be improved by diffusional resistance***

- For **series or consecutive reactions**,

$$A \xrightarrow{k_1} B \ (desired) \xrightarrow{k_2} D$$
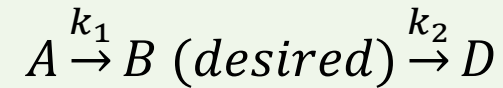
Selectivity $\quad S_P = \dfrac{net\ rate\ of\ production\ of\ B}{rate\ of\ disappearance\ of\ A} = \dfrac{r_B}{r_A} = \dfrac{dC_B}{-dC_A} = \dfrac{k_1 C_{As} - k_2 C_{Bs}}{k_1 C_{As}} = 1 - \dfrac{k_2}{k_1} \cdot \dfrac{C_{Bs}}{C_{As}}$

- Selectivity will vary with position in the pellet as $\dfrac{C_B}{C_A}$ changes

- Diffusion resistances causes C_A to decrease while going from the outer surface towards the centre of the pellet

- Since B is formed within the pellet and must diffuse outwards to enter the bulk stream, C_B increases towards the pellet centre

- Thus from the above equation it can be seen that *changes in A (low C_A) and B (high C_B) both act to reduce the selectivity of B*

- Quantitatively, for strong pore diffusional resistance

$$\text{Selectivity} = \dfrac{\left(k_1/k_2\right)^{1/2}}{1 + \left(k_1/k_2\right)^{1/2}}$$