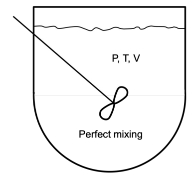
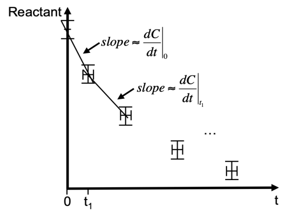
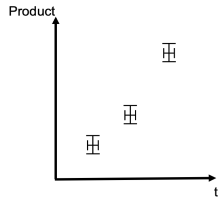
A General Overview of the Class

You want to study a RX: A → B

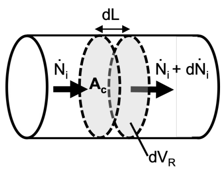
1) Measure r_{obs}:







$$\left.\frac{dC}{dt}\right|_0 = r(t=0) = r(C_{A,0})$$



$$For\ small\ X_i\ (< 5\%) \quad \rightarrow \dot{N}_i^0 \left.\frac{dX_i}{dV_R}\right|_{V_R=0} \approx \dot{N}_i^0 \frac{\Delta X_i}{V_R} \approx -\upsilon_i r\Big|_{C_{i,0}}$$

Make sure to use what you learned about non-ideal reactors to make sure these reactors are quasi-ideal!

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A General Overview of the Class

You want to study a RX: A → B

2) You have r_{obs} but what is r_{max} (the true kinetic *r*)?

$$\eta_0 = \frac{r_{obs}}{r_{max}} \rightarrow r_{max} = \frac{r_{obs}}{\eta_0}$$

3) You use. $r_{max} = f(C_A, C_B \ldots)$ for figuring out a mechanism:

Proposed mechanism:

e.g. $r_{max} = \frac{cst1[A]}{1 + cst2[B]}$

(1) $A + * \xrightarrow{k_1} A^*$

(2') $A^* \overset{K_2'}{\rightleftharpoons} B + *$

$\rightarrow r = \frac{k_1[A][*]_0}{1 + K_2[B]}$

You use this *r* to predict the r_{obs} in a future large reactor and design the reactor.

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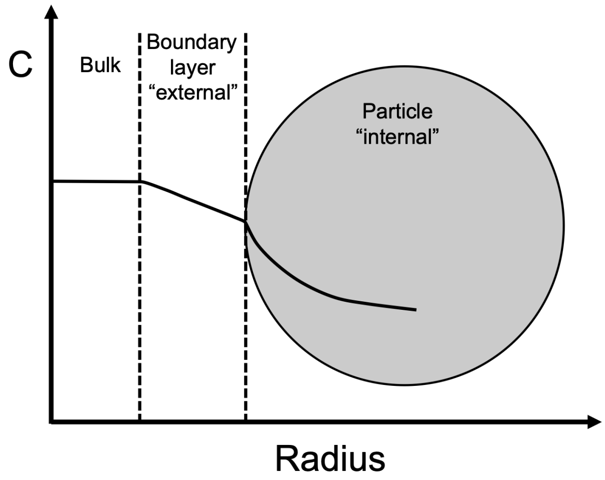
Summary of transport transfer effects

The overview of mass transfer:



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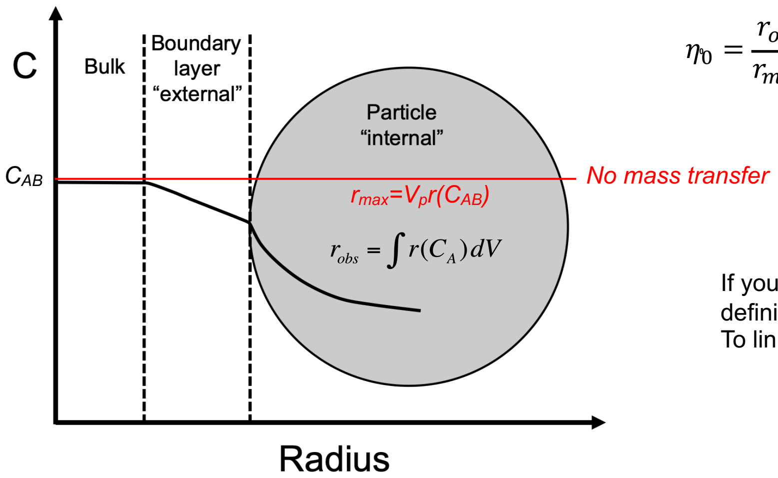
Summary of transport transfer effects

The effectiveness factor η:

Characterizes the ratio of the *observed* rate over the *intrinsic* rate (observed in the absence of mass transfer)



$$\eta_0 = \frac{r_{obs}}{r_{max}} = \frac{S_P \int_0^{x_p} r(C_A)\,dx}{V_p r(C_{AB})}$$

If you use C_{AB} (instead of C_{AS}) in the definition of η, you usually write η_0. To link the two, we have:

$$\eta_0 = \eta_{external}\eta_{internal} = \bar{\eta}\eta$$

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Summary of transport effects

Combined heat and mass transfer effects

In cases where the reaction releases (exothermic) or consumes (endothermic) heat. Heat transfer must be studied because different local T° can change local kinetics (by Arrhenius: $k(T) = \bar{A}exp\left(\frac{-E_a}{RT}\right)$) and dramatically affect the global kinetics.

To do so, we have to simultaneously solve the mass and energy balance. For example, with a slab and a 1st order reaction:

Mass balance:

$$-\frac{d\dot{n}_A}{dx} = k(T)\, C_A$$

In-Out -Source

Energy balance:

$$-\frac{d\dot{q}}{dx} = \Delta H_r\, k(T)\, C_A$$

(In-Out) -Source

$$\frac{d^2 C_A'}{d\chi^2} = \phi^2 \exp\left[-\gamma\left(\frac{1}{T'} - 1\right)\right] C_A'$$

$$\frac{d^2 T'}{d\chi^2} = -\phi^2\, \beta\, \exp\left[-\gamma\left(\frac{1}{T'} - 1\right)\right] C_A'$$

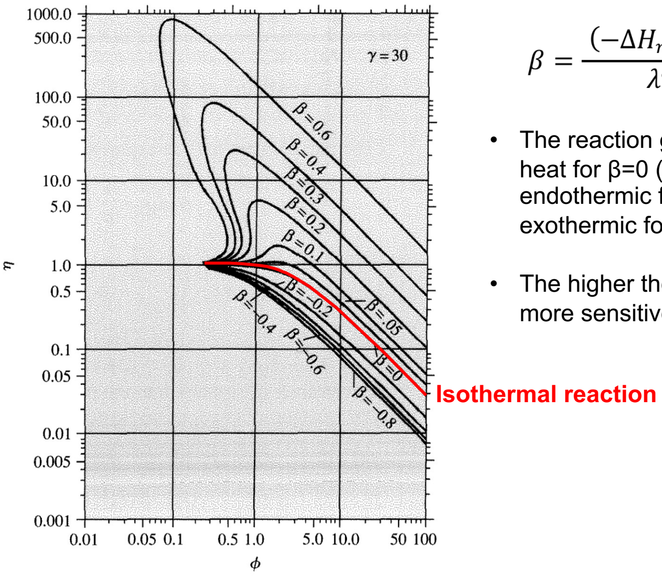
Boundary conditions:

$$C_A' = T' = 1 \quad @\ \chi = 1$$

$$\frac{dC_A'}{d\chi} = \frac{dT'}{d\chi} = 0 \quad @\ \chi = 0$$

3.3.4 Internal heat transfer effects (continued)

Solved numerically for a sphere:



$$\beta = \frac{(-\Delta H_r) D_{TA}^e\, C_{AS}}{\lambda^e\, T_S}$$

- The reaction generates no heat for β=0 (isothermal RX), endothermic for β<0 and exothermic for β>0
- The higher the value of γ, the more sensitive you are to T°

3.5 Analysis of rate data

3.5.1 Criteria analysis

- No significant internal (intraphase) diffusion effects are seen (*η≥0.95*) if:

Observed rate per unit volume

$$\frac{r_{obs}R_p^2}{C_{AS}D_{TA}^e} < 1 \quad \text{or} \quad \frac{r_{obs}R_p^2}{C_{AS}D_{TA}^e} < 1/n$$ For reaction order n > 0

- No significant external (interphase) diffusion effects are seen (*η≥0.95*) if:

$$\frac{r_{obs}R_p}{C_{AB}\bar{k}_c} < 0.15/n$$ For reaction order n > 0

Notice that the criteria is analogous to those for internal transport where $\bar{k}_c$ replaces D_{TA}^e / R_p .

These criteria are known as the *Weisz-Prater criteria*.

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3.5 Analysis of rate data

3.5.1 Criteria analysis

For heat transfer, the *Anderson criteria* can be used.

- No significant internal (intraphase) heat effects are seen (*k(T)* within 5% of *k(T_S)*) if:

$$\frac{|\Delta H_r| r_{obs}R_p^2}{\lambda^e T_S} < 0.75\frac{RT}{E_a}$$

- No significant external (interphase) diffusion effects are (*k(T)* within 5% of *k(T_S)*) if:

$$\frac{|\Delta H_r| r_{obs}R_p}{h_t T_B} < 0.15\frac{RT}{E_a}$$

Again the criteria is analogous to that for internal heat transfer where h_t replaces λ^e / R_p .

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3.5 Analysis of rate data

3.5.2 Madon-Boudart rules

The limitations of these criteria is that they require parameters like: D_{TA}^{e} $\bar{k}_c$ h_t λ^e

These parameters are empirical and catalyst dependent and can even change within the pellet.

The Madon-Boudart rule provides a simple experimental test to detect mass transfer limitations:

@ T_1: Measure TOF at catalyst loading 1 | Measure TOF at catalyst loading 2

Are they the same? No → Mass transfer and/or heat transfer limitations

Yes ↓

@ T_2: Measure TOF at catalyst loading 1 | Measure TOF at catalyst loading 2

Are they the same? No → Mass and/or heat transfer limitations

Yes ↓

No mass or heat transfer limitations

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3.5 Analysis of rate data

3.5.2 Madon-Boudart rules

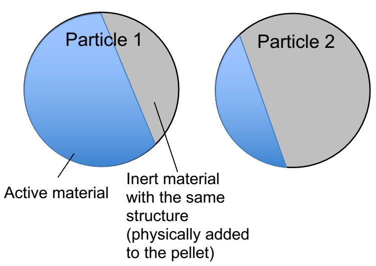
The principle: *the intrinsic turnover frequency (TOF) should not depend on the concentration of active sites.*

Reminder: TOF= $r_t = \frac{1}{\bar{S}}\frac{dn}{dt}$

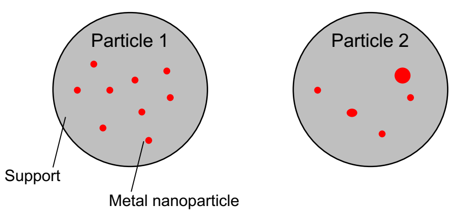
Nb of active sites (measured by chemisorption)

Preparing catalyst with different loadings:

By dilution:



Varying metal loading:



Direct comparison is possible by measuring $\bar{S}$

$\bar{S}$ should be measured by chemisorption because dispersion could be different.

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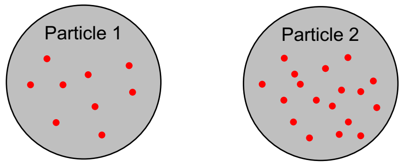
3.5 Analysis of rate data

3.5.2 Madon-Boudart rules

Why does this work?

In this example we should see double the rate in particle 2 compared to particle 1 if TOF and dispersion are constant.



Initial loading Double loading

- If external mass transfer limitations control the process it will change very little because the rate will be proportional to the pellet surface.
- If internal mass transfer limitations control the process, the rate will not double because, in particle 2, the reactant will be consumed closer to the surface and the particles in the interior will contribute less to the rate than in particle 1.
- We always check more than 1 temperature to exclude the possibility that heat transfer limitations is making the rates appear similar.

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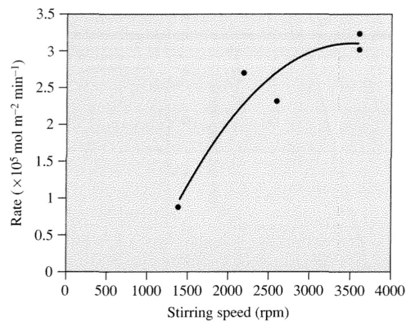
3.5 Analysis of rate data

3.5.3 Other tests

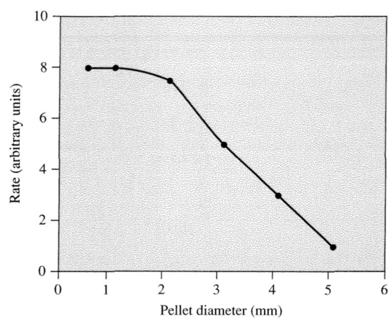
Other tests that can be performed include:

Varying stirring speed or flow rate:



Easy but not 100% indicative of the absence of heat or mass transfer (especially internal effects).

Varying pellet size:



More definitive but typically more difficult and can lead to high pressure drop.

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