Catalyst Deactivation

Rate equation for deactivation from experiment

- Experimental devices for studying deactivating catalysts fall into two classes – those using a batch of solids and those using a through flow of solids

- If deactivation is slow, a batch mode may be used whereas a continuous flow is required for a fast reaction (rapid deactivation)
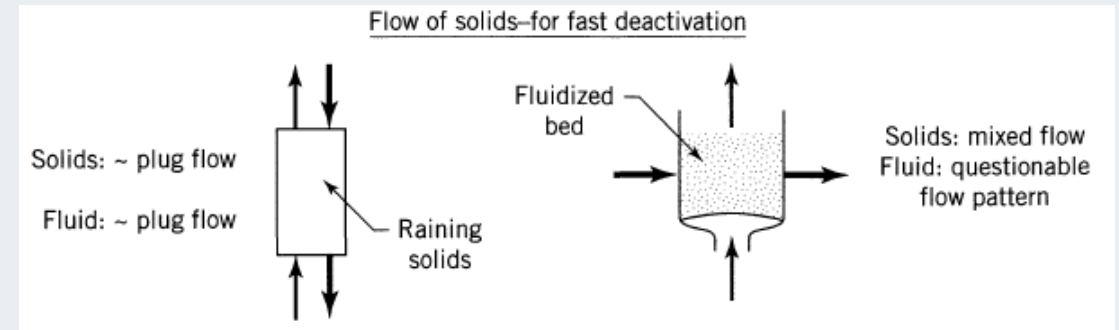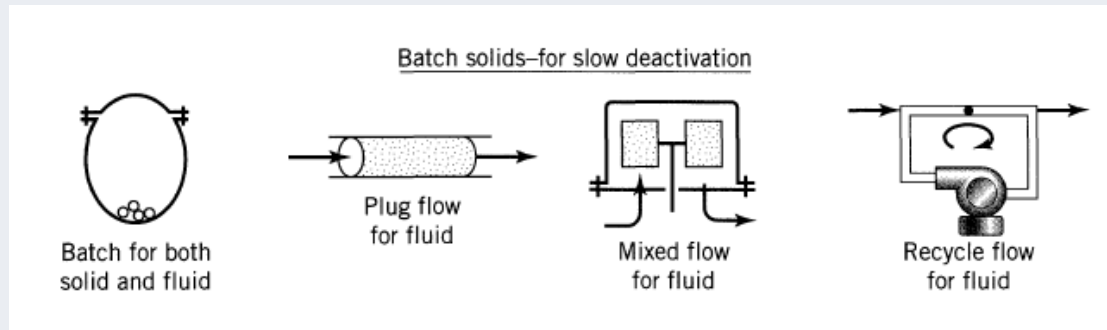
- The method for searching for a rate equation is analogous to that of homogeneous reactions – starting with the simplest kinetic form and checking if it fits the data

- The main complication is the extra factor of activity

- Batch solid reactors are more commonly used and the type of reactors used depends on whether the deactivation is concentration dependent or not

- If yes, a reactor in which C_A is forced to stay unchanged with time is used. Other wise for concentration independent reactions, any type of reactor can be used

Determining rate for independent deactivation – Batch solids

Here it is seen how to interpret experiments from the various batch-solids reactors and how to manipulate the basic performance equations for these reactors by testing the fit for cases of independent deactivation

$$-r_A = kC_A a$$ First order reaction

$$-\frac{da}{dt} = k_d a$$ First order, concentration independent deactivation

Batch-solid, Batch – fluid

• The relation between changing gas concentration and time is determined

$$-\frac{dC_A}{dt} = \frac{W}{V}\left(-\frac{1}{W}\frac{dN_A}{dt}\right) = \frac{W}{V}(-r_A) = \frac{W}{V}kC_A a$$

$$-\frac{da}{dt} = k_d a$$

Integrating we have, $$a = a_o e^{-k_d t}$$

For unit initial activity, $$a = e^{-k_d t}$$

Replacing in above equation,

$$-\frac{dC_A}{dt} = \frac{W}{V}kC_A e^{-k_d t}$$

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = \frac{W}{V}k \int_0^t e^{-k_d t}\, dt$$

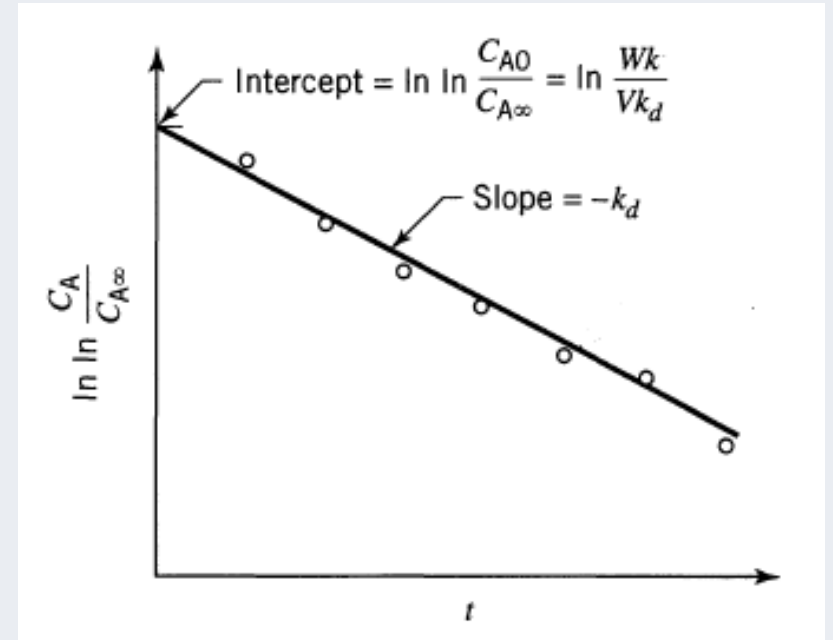$$\ln\frac{C_{Ao}}{C_A} = \frac{Wk}{Vk_d}\left(1 - e^{-k_d t}\right)$$

At $t = \infty$, $\qquad \ln\frac{C_{Ao}}{C_{A\infty}} = \frac{Wk}{Vk_d}$

Combining the we have, $\qquad \ln\frac{C_{Ao}}{C_A} - \ln\frac{C_{Ao}}{C_{A\infty}} = \frac{Wk}{Vk_d} - \frac{Wk}{Vk_d}e^{-k_d t} - \frac{Wk}{Vk_d}$

$$\ln\frac{C_A}{C_{A\infty}} = \frac{Wk}{Vk_d}e^{-k_d t}$$

$$\ln\left(\ln\frac{C_A}{C_{A\infty}}\right) = \ln\left(\frac{Wk}{Vk_d}\right) - k_d t$$

This type of reaction is used if the characteristic times for reaction and deactivation are of the same order of magnitude

Batch-solid, Mixed constant flow of fluid (MFR)

For MFR, $\boxed{\tau = \dfrac{W C_{Ao}}{F_{Ao}} = \dfrac{W}{v} = \dfrac{C_{Ao} - C_A}{k C_A a}}$

Pseudo steady state assumption
Batch of solids $-$ slow deactivation
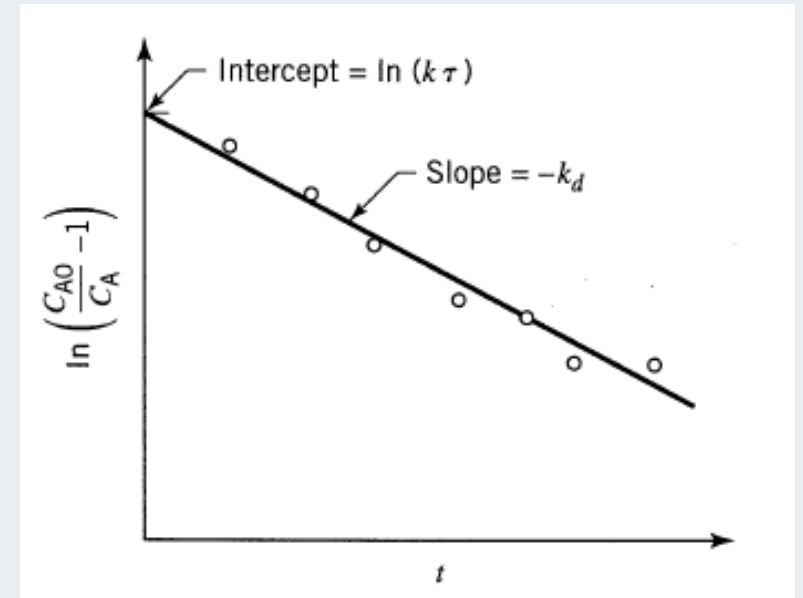
or, $k\tau a = \dfrac{C_{Ao}}{C_A} - 1$

$$\boxed{\dfrac{C_{Ao}}{C_A} = 1 + k\tau a}$$

Now, $a = e^{-k_d t}$ (derived earlier for independent deactivation)

$$\dfrac{C_{Ao}}{C_A} = 1 + k\tau e^{-k_d t}$$

$$\boxed{ln\left(\dfrac{C_{Ao}}{C_A} - 1\right) = ln(k\tau) - k_d t}$$

Intercept = ln $(k\tau)$

Slope = $-k_d$

$ln\left(\dfrac{C_{AO}}{C_A} - 1\right)$

t

Expression shows how reactant concentration at the outlet rises with time

Batch-solid, Mixed changing flow of fluid (to keep C_A fixed)

For steady flow in a MFR,
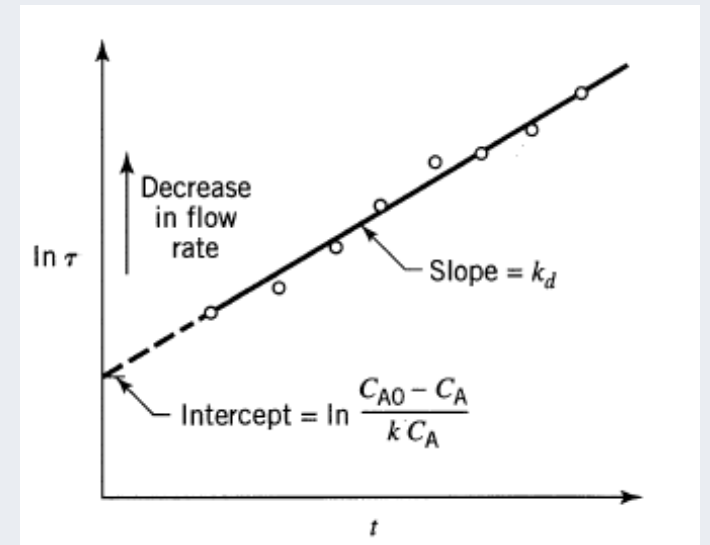$$\frac{C_{Ao}}{C_A} = 1 + k\tau e^{-k_d t}$$

Pseudo steady state assumption (conditions change slowly enough for the system to be at steady state at all times

To keep C_A constant, the flow rate must be slowly changed with time

Flowrate is lowered as the catalyst deactivates

$$\frac{1}{k}\left(\frac{C_{Ao}}{C_A} - 1\right) = \tau e^{-k_d t}$$

$$ln\left(\frac{C_{Ao} - C_A}{kC_A}\right) = ln\tau - k_d t$$

$$ln\tau = k_d t + ln\left(\frac{C_{Ao} - C_A}{kC_A}\right)$$

If the deactivation kinetics are calculated for an independent deactivation condition, then there is **no** particular advantage of using the above mode of variable flow as concentration does not influence deactivation

However, for other deactivation kinetics, this mode of operation helps to decouple the three factors – concentration, temperature and activity and study them a pair at a time

Batch-solid, Plug constant flow of fluid (PFR)

For PFR, the performance equation is

$$\frac{W}{F_{Ao}} = \int \frac{dX_A}{(-r_A)} = \int \frac{dX_A}{kC_A a} = \frac{1}{ka}\int \frac{dX_A}{C_A}$$

$$\frac{W}{F_{Ao}} = \frac{1}{ka}\int \frac{dX_A}{C_A} = \frac{1}{ka}\int_0^{X_A} \frac{dX_A}{(1-X_A)C_{Ao}} = -\frac{1}{kC_{Ao}a}ln(1-X_A)$$

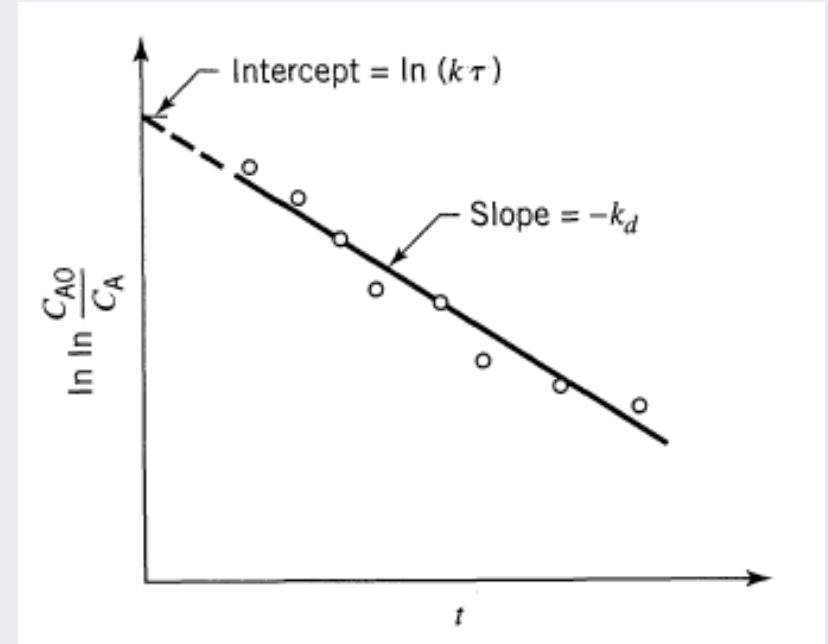$$\frac{W}{F_{Ao}} = \frac{1}{kC_{Ao}a}\,ln\frac{C_{Ao}}{C_A}$$

$$\frac{WC_{Ao}}{F_{Ao}} = \tau = \frac{1}{ka}\,ln\frac{C_{Ao}}{C_A}$$

$$\tau = \frac{1}{ke^{-k_d t}}\,ln\frac{C_{Ao}}{C_A}$$
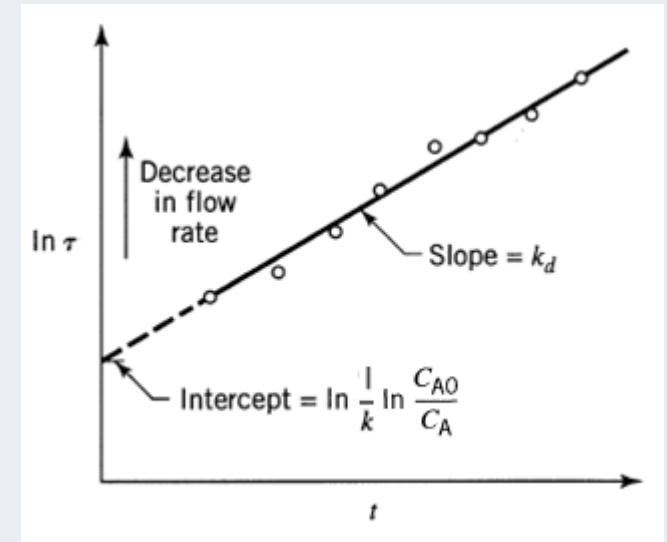
$$ln\frac{C_{Ao}}{C_A} = k\tau e^{-k_d t}$$

$$ln\left(ln\frac{C_{Ao}}{C_A}\right) = ln(k\tau) - k_d t$$

Intercept = ln (kτ)

Slope = −k_d

ln ln $\frac{C_{AO}}{C_A}$

t

Batch-solid, Plug changing flow of fluid (to keep $C_{A,out}$ fixed)

For steady flow in a PFR, $\tau = e^{k_d t} \dfrac{1}{k} ln \dfrac{C_{Ao}}{C_A}$

$$ln\tau = k_d t + ln\left(\frac{1}{k} ln \frac{C_{Ao}}{C_A}\right)$$

Example

A reaction $A \rightarrow B$ is studied at temperature T in a basket reactor (batch solids and mixed flow of gas) in which the gas composition is kept unchanged, despite deactivation of catalyst. What can you say about the rates of reaction and deactivation? To keep the gas concentration in the reactor unchanged, the flow rate of reactant has to be lowered to 5% of the initial value

Run 1	C_{Ao} = 1 mol/l X_A = 0.5	t, time from start of run, h	0	1	2	3
		τ, gcat.min/l	1	e	e^2	e^3

Run 2	C_{Ao} = 2 mol/l X_A = 0.667	t, time from start of run, h	0	1	2	3
		τ, gcat.min/l	2	$2e$	$2e^2$	$2e^3$

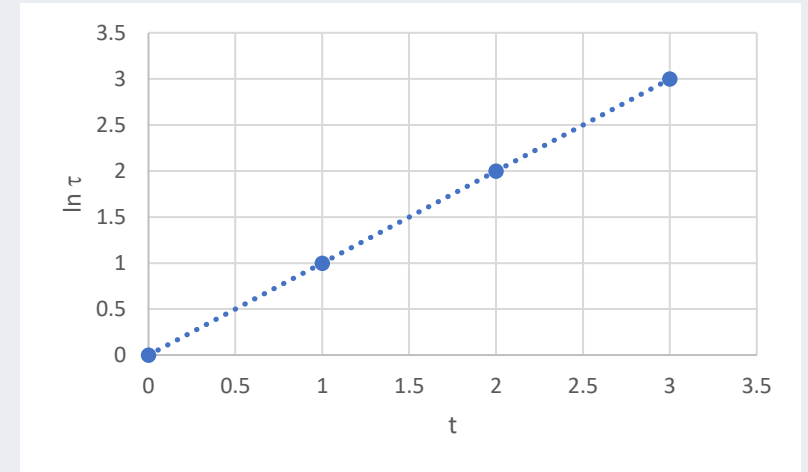For a MFR with changing flow (to keep C_A fixed) and batch solids, $\dfrac{C_{Ao}}{C_A} = 1 + k\tau e^{-k_d t}$ and

$$ln\,\tau = k_d t + ln\left(\frac{C_{Ao}-C_A}{kC_A}\right)$$

<u>For Run 1</u>

C_{Ao} = 1 mol/l X_A = 0.5	t,	0	1	2	3
	τ	1	e	e^2	e^3
	ln τ	0	1	2	3

Intercept = 0 = $ln\left(\frac{C_{Ao}-C_A}{kC_A}\right)$, $\therefore \dfrac{C_{Ao}-C_A}{kC_A} = 1$

$C_{Ao} = 1$ mol/l $C_A = 0.5$ mol/l , $\therefore k = \dfrac{1-0.5}{0.5} = 1$ and slope = k_d = 1

<u>For Run 2</u>
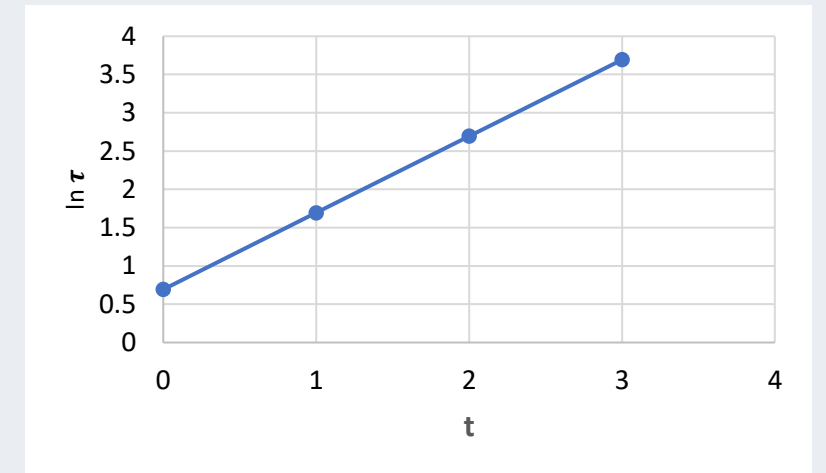
C_{Ao} = 2 mol/l X_A = 0.667	t,	0	1	2	3
	τ	2	$2e$	$2e^2$	$2e^3$
	ln τ	0.693	1.693	2.693	3.693

Intercept = 0.693 = $ln\left(\frac{C_{Ao}-C_A}{kC_A}\right)$, $C_{Ao} = 2$ mol/l, $C_A = 0.666$ mol/l ,

$\therefore k = \dfrac{2-0.666}{0.666 \times 2} = 1$ slope = k_d = 1

For both cases, $k = 1$ and k_d = 1 $-r_A = C_A a$ $-\dfrac{da}{dt} = a$