Lecture # 12 CHE331A

- Introduction and design equation for ideal reactors
- Basics of reaction kinetics and Isothermal reactor design - conversions, molar flow rates or concentrations
- Differential, Integral, Initial Rates, Half Life, Non-linear regression method of Analysis
- Differential PBR method of Collection/Analysis

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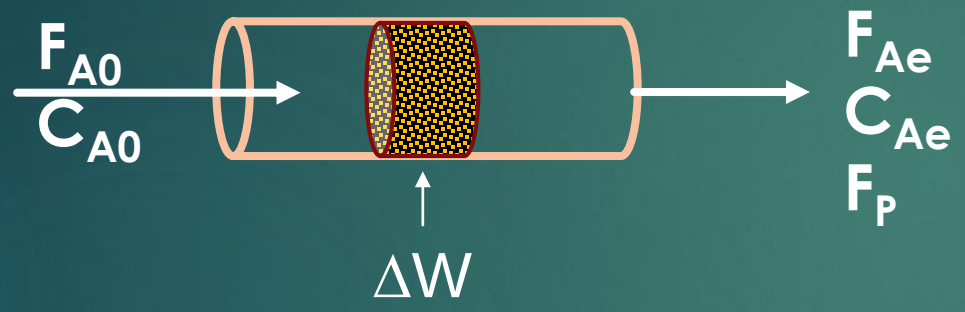
Methanator

$3H_2 + CO = CH_4 + H_2O$

Differential reactor is used to determine rate as a function of concentration or partial pressure

- Consist of a tube containing a small amount of catalyst



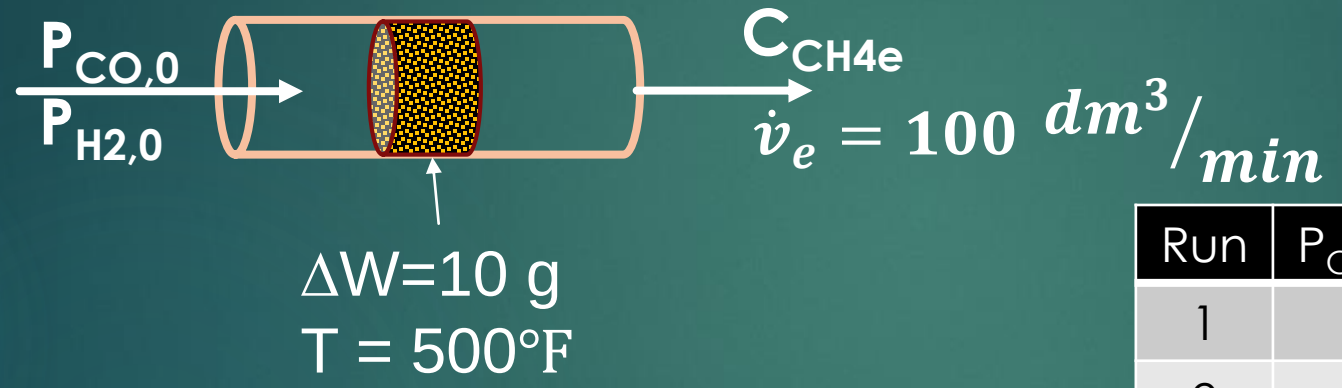
$$F_{A0} - F_{Ae} + r_A' \Delta W = 0$$

$$-r_A' = \frac{F_{A0} - F_{Ae}}{\Delta W}$$

- In terms of concentration: $-r_A' = \frac{\dot{v}_0 C_{A0} - \dot{v}.C_{Ae}}{\Delta W} = \frac{\dot{v}_0 (C_{A0} - C_{Ae})}{\Delta W}$
- In terms of conversion or product molar flow rate: $-r_A' = \frac{X F_{A0}}{\Delta W} = \frac{\mu_P F_P}{\Delta W}$
  - Thus, rate can be determined as a function of C_{A0}

Differential reactor is used to develop rate laws and determine parameter values – Example 5-5

- $3H_2 + CO \rightarrow CH_4 + 2H_2O$ methanation reaction; Convert CO



(a) relate the rate to $C_{CH4,e}$

(b) assumed: $r'_{CH4} = f(CO).g(H_2)$

(c) determine rate law dependency and rate law parameters

Run	P_{CO} (atm)	P_{H2} (atm)	C_{CH4} (mol/dm³)
1	1.00	1.0	**$1.73*10^{-4}$**
2	1.80	1.0	**$4.40*10^{-4}$**
3	4.08	1.0	**$10.0*10^{-4}$**
4	1.00	0.1	**$1.65*10^{-4}$**
5	1.00	0.5	**$2.47*10^{-4}$**
6	1.00	4.0	**$1.75*10^{-4}$**

Outlet concentration given not $C_{CO,0}$

Rate of methane formation can be determined and related to rate of CO disappearance

- In terms of conversion or product molar flow rate: $-r'_A = \frac{XF_{A0}}{\Delta W} = \frac{\mu_P F_P}{\Delta W}$
- $3H_2 + CO \rightarrow CH_4 + 2H_2O$ $\quad -r'_{CO} = r'_{CH4} = \frac{F_{CH4}}{\Delta W} = \frac{\dot{v}_e C_{CH4}}{\Delta W}$
- Thus, $-r'_{CO}$ can be determined
- For example, for run 1

$$r'_{CH4} = \left(\frac{300\ dm^3}{min}\right)\frac{1.73*10^{-4} mol/dm^3}{10\ g\ cat}$$

$$r'_{CH4} = 5.2 * 10^{-3}\left(\frac{mol\ CH_4}{g.cat*min}\right) = -r'_{CO}$$

Run	P_{CO} (atm)	P_{H2} (atm)	C_{CH4} (mol/dm³)	r'_{CH4} $\left(\frac{mol\ CH_4}{g.cat * min}\right)$
1	1.00	1.0	$1.73*10^{-4}$	**$5.2*10^{-3}$**
2	1.80	1.0	$4.40*10^{-4}$	**$13.2*10^{-3}$**
3	4.08	1.0	$10.0*10^{-4}$	**$30.0*10^{-3}$**
4	1.00	0.1	$1.65*10^{-4}$	**$4.95*10^{-3}$**
5	1.00	0.5	$2.47*10^{-4}$	**$7.42*10^{-3}$**
6	1.00	4.0	$1.75*10^{-4}$	**$5.25*10^{-3}$**

Proper planning of the experiments assist in determining the form of the rate law

- $r'_{CH4} = f(CO).g(H_2)$ for runs 1,2 and 3 P_{H2} is constant and P_{CO} increases $\rightarrow$ $r'_{CH4} = kP^{\alpha}_{CO}.g(H_2) = k'P^{\alpha}_{CO}$
- Taking natural log we have $ln(r'_{CH4}) = lnk' + \alpha.ln(P_{CO})$
- By plotting for the first three runs
- $\alpha = 1.22 \approx 1.00$

  (more runs would help)
- Thus, $r'_{CH4} = k.P_{CO}.g(H_2)$
- We need to find the dependency of rate with hydrogen

Run	P_{CO} (atm)	P_{H2} (atm)	C_{CH4} (mol/dm^3)	r'_{CH4} $\left(\frac{mol\ CH_4}{g.cat * min}\right)$
1	**1.00**	**1.0**	**$1.73*10^{-4}$**	**$5.2*10^{-3}$**
2	**1.80**	**1.0**	**$4.40*10^{-4}$**	**$13.2*10^{-3}$**
3	**4.08**	**1.0**	**$10.0*10^{-4}$**	**$30.0*10^{-3}$**
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Rate dependency on P_{H2} non-monotonic

- Dependency of r'_{CH4} with P_{H2} cannot be represented by a power law
- With increasing P_{H2}
  - Rate increases (run 4 to run 5)
  - Low P_{H2}

$$r'_{CH4} \sim P_{H2}^{\beta 1}$$

  - High P_{H2}; decreases (run 5 to run 1)

$$r'_{CH4} \sim \frac{1}{P_{H2}^{\beta 2}}$$

  - Even higher P_{H2}; rate is relatively constant (run 1 to run 6)

Run	P_{CO} (atm)	P_{H2} (atm)	C_{CH4} (mol/dm³)	r'_{CH4} $\left(\frac{mol\ CH_4}{g.cat * min}\right)$
1	**1.00**	**1.0**	**$1.73*10^{-4}$**	**$5.2*10^{-3}$**
2	1.80	1.0	$4.40*10^{-4}$	$13.2*10^{-3}$
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There should be one Rate law to be consistent with the experimental observations

- Rate variations depends on P_{H2} $\quad r'_{CH4} \sim P_{H2}^{\beta 1}$ at low P_{H2}, and

  $r'_{CH4} \sim \frac{1}{P_{H2}^{\beta 2}}$ at high P_{H2}

- One such rate law is: $\quad r'_{CH4} \sim \frac{P_{H2}^{\beta 1}}{1 + b.P_{H2}^{\beta 2}}$ (such forms are common)
- Does this rate law satisfies the observed trends?
- At low P_{H2} the denominator $\rightarrow 1$ $\quad$ and $r'_{CH4} \sim P_{H2}^{\beta 1}$
- At high P_{H2} the denominator $\rightarrow b.P_{H2}^{\beta 2}$ $\quad$ and $r'_{CH4} \sim \frac{P_{H2}^{\beta 1}}{P_{H2}^{\beta 2}} \sim \frac{1}{(P_{H2})^{\beta 2 - \beta 1}}$

$\beta 2 > \beta 1$

Non-linear regression is useful to determine the parameters

- Taking into account the variation of rate with P_{CO}, the "unified" rate law is

$$r'_{CH4} = \frac{aP_{CO}P_{H2}^{\beta 1}}{1 + b.P_{H2}^{\beta 2}}$$

- Need to find the rate law parameters $a, b, \beta 1\ and\ \beta 2$, which is consistent with the experimental data
- Done by non-linear regression, e.g., initial guess for the parameters = 1
- Resulting rate law with only six runs (N=6 and K=4)

$$r'_{CH4} = \frac{0.025P_{CO}P_{H2}^{0.61}}{1 + 2.49 * P_{H2}}$$

Rate law for the methanation reaction – additional considerations

- The rate law for the methanation reaction: $3H_2 + CO \rightarrow CH_4 + 2H_2O$

$$r'_{CH4} = \frac{0.025 P_{CO} P_{H2}^{0.61}}{1 + 2.49 * P_{H2}}$$

- Heterogeneous catalysis, power associated with H_2 is ½ (dissociation adsorption)
- Consider a factor of ½, instead of 0.61, and evaluate 2 parameters $a\ and\ b$
- Again by non-linear regression, with initial guess for $a\ and\ b$ as those obtained previously, and with P_{CO} and P_{H2} in atm

$$r'_{CH4} = \frac{0.018 P_{CO} P_{H2}^{0.5}}{1 + 1.49 * P_{H2}} \frac{mol}{g.cat * s}$$