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# Calculation of the Rate Constant.

<u>Henry's Constant</u>: (Nevelhoff et. al., 1985)

For $H_2$, $$\boxed{H_{H_2} = 6.952\, e^{555.1/T} \quad \left(\frac{MPa \cdot dm^3}{mol}\right)}$$

when T is in K

$T = 256\ °C = 538.15\ K$

$$H_{H_2} = 19.508 \quad \left(\frac{MPa\ dm^3}{mol}\right)$$

<u>Const.</u>

From the plot. Let $f(x_{H_2}) = Y$ dimensionless

$$\frac{1}{Q^\circ} = X \quad \left(\frac{hr \cdot gFe}{nl}\right)$$

$$Y = Const.\ X$$

Take two points: $(X, Y) = (0.833, 1.55), (0.2, 0.4)$

$$Const. = \frac{\Delta Y}{\Delta X} = \frac{1.55 - 0.4}{0.833 - 0.2} = 1.817$$

$$\boxed{Const. = 1.817 \left(\frac{nl}{hr\ gFe}\right)}$$

(2)

- Note the volume used is "nl" — liter at normal condition. It needs to be converted to the volume at Rx condition:

| | P | T |
|---|---|---|
| ⓐ Normal Cond. | 1atm = 14.696 psia | 20°C = 293.15 K |
| ⓑ Rx. Cond | 290 psig = 304.696 psia | 265°C = 538.15 K |

By $PV = nRT$

$$\frac{P_{ⓐ} V_{ⓐ}}{P_{ⓑ} V_{ⓑ}} = \frac{T_{ⓐ}}{T_{ⓑ}}$$

$$\therefore \quad V_{ⓑ} = \frac{P_{ⓐ}}{P_{ⓑ}} \frac{T_{ⓑ}}{T_{ⓐ}} V_{ⓐ}$$

$$= \frac{14.696}{304.696} \frac{538.15}{293.15} V_{ⓐ} = 0.0885 \ V_{ⓐ}$$

$$\therefore \quad Const. = 1.817 \times 0.0885 \left(\frac{l}{hr\ gFe}\right)$$

$$\boxed{Const. = 0.161 \left(\frac{l}{hr\ gFe}\right)}$$

• Rate Constant k

$$f(x_{H_2}) = \text{Const.} \times \left(\frac{1}{Q^\circ}\right)$$

$$\text{Const.} = \frac{k\,RT}{H_{H_2}\left(1+\frac{1}{U}\right)}$$

$$\therefore \boxed{k = \text{Const.} \cdot \frac{H_{H_2}\left(1+\frac{1}{U}\right)}{RT}}$$

$U = 0.578$ $\quad R = 8.314 \left(\frac{J}{mol\ K}\right)$

$$k = 0.161 \left(\frac{l}{hr\ gFe}\right) \times \frac{19.508 \left(\frac{MPa\ dm^3}{\cancel{mol}}\right)\left(1+\frac{1}{0.578}\right)}{8.314 \left(\frac{J}{\cancel{mol}\ \cancel{K}}\right) \cdot 538.15 (\cancel{K})}$$

$$= 1.916 \times 10^{-3} \left(\frac{l\ MPa\ dm^3}{hr\ gFe \cdot J}\right)$$

Note $\quad MPa\ dm^3 = 10^6 \frac{N}{m^2} 10^{-3} m^3$

$$= 10^3\ Nm = 10^3\ J$$

$$\therefore k = 1.916 \times 10^{-3} \frac{10^3 \cancel{J}\ l}{hr\ gFe\ \cancel{J}} = 1.916 \frac{l}{hr\ gFe}$$

$$\text{or } \boxed{k = 0.532 \left(\frac{cm^3}{s \cdot gFe}\right)}$$

Comparison with Data in Literatures

If ignore the effect of $CO_2$, the data by Ledakowicz et al. (1985) gives,

1.3% K. in Cat.

| T (K) | (°C) | k $\left(\frac{cm^3}{s \cdot g\,Cat.}\right)$ |
|---|---|---|
| 493 | 220 | 0.161 |
| 513 | 240 | 0.428 |
| 523 | 250 | 0.836 |
| 533 | 260 | 0.965 |

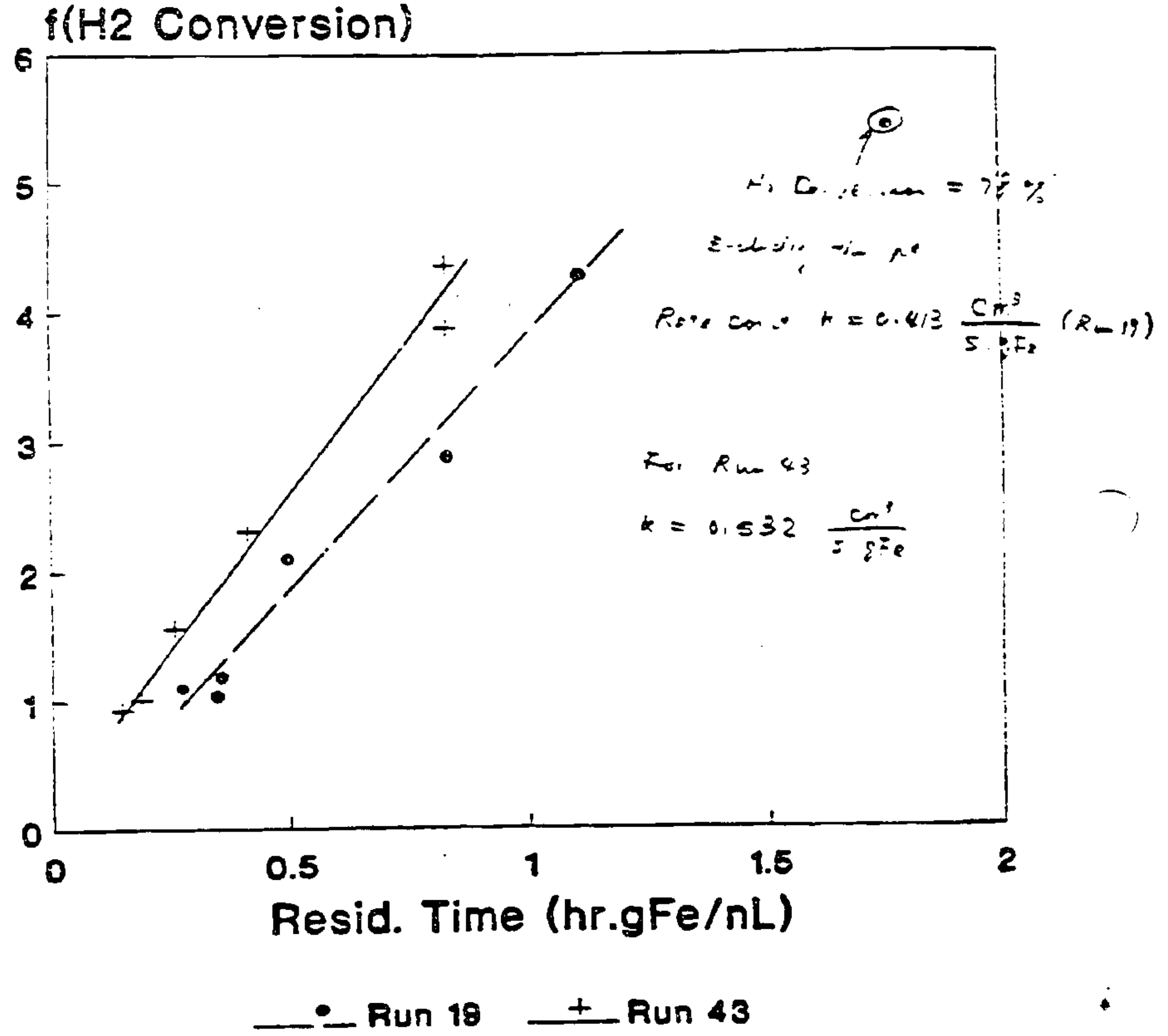
UCP data:

| | | |
|---|---|---|
| 538 | 265 | 0.532 $\left(\frac{cm^3}{s \cdot g\,Fe}\right)$ |

do [illegible] your [illegible] calc.

Did you compare [illegible] Ledakowicz [illegible] [illegible]

# CSTR MODEL:PLANT 700B TESTS
# f(H2 Conv.) vs. Residence Time



$H_2$ Conversion = 78 %

Excluding this pt

Rate const $k = 0.413 \frac{cm^3}{s\ gFe}$ (Run 19)

For Run 43

$k = 0.532 \frac{cm^3}{s\ gFe}$

265 C, Alpha=-0.5

[illegible]

| | Feed Rate (mL/[illegible]) | 1/Feed Rate | $x_w$ | $f(x_w)$ | Feed Rate (mL/h [illegible]) | 1/Feed Rate |
|---|---|---|---|---|---|---|
| 1. | 0.059 | 16.9 | 78 | 5.417 | 0.57 | 1.756 |
| 2 | [illegible] | 11.62 | 78 | 4.465 | 0.90 | 1.111 |
| 3. | 0.115 | 8.77 | 65 | 2.878 | 1.25 | 0.833 |
| 4. | [illegible] | [illegible] | 55 | 2.053 | 2.0 | 0.5 |
| 5 | [illegible] | [illegible] | 51 | 1.197 | 2.8 | 0.357 |
| 6. | [illegible] | 3.62 | 39 | 1.663 | 2.9 | 0.345 |
| 7. | [illegible] | 3.9 | 36 | 1.025 | 3.60 | 0.278 |

[illegible]

| | $f(x_w)$ | Feed Rate (mL/[illegible]) | 1/Feed Rate |
|---|---|---|---|
| 72 | 3.875 | 1.2 | 0.833 |
| [illegible] | 4.36 | 1.2 | 0.833 |
| 55 | 2.51 | 2.4 | 0.417 |
| 45 | 1.56 | 3.8 | 0.263 |
| 21 | 1.01 | 5.2 | 0.192 |
| 29 | 0.93 | 6.7 | 0.149 |

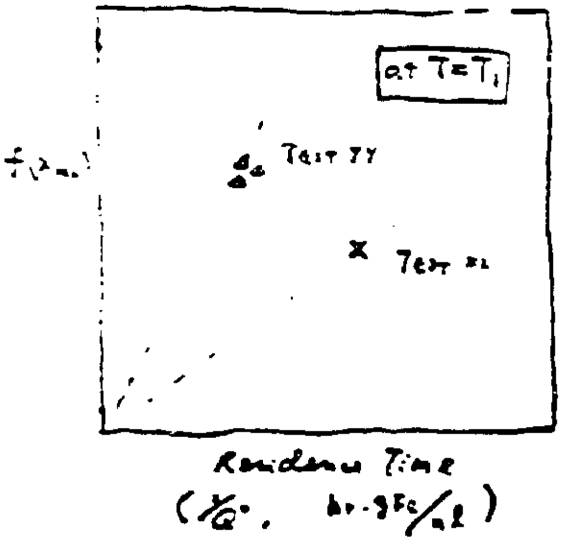
## About a single test or a few tests at similar conditions:

### Ⓐ Rate Constant

If we assume:

- 1st order reaction (w.r.t. $H_2$)
- Conversion ⟶ 0 as feed rate ⟶ ∞

Then a single test can be used in conjunction with the CSTR model to find the rate constant:



$$f(x_{H_2}) = \frac{k\,RT}{H_{H_2}\,\dot{Q}^{\circ}}$$

## Ⓔ Activation Energy.

Rate constant is usually expressed as a function of T:

$$k = a\, e^{-\frac{b}{RT}}$$

where b is called activation energy.

Then CSTR Model gives

$$f(X_{HL}) = \frac{a\, e^{-\frac{b}{RT}}\, RT}{a_1\, e^{\frac{b_1}{T}}\, \dot{Q}^\circ} = \left(\bar{A}\, e^{-\frac{\bar{B}}{T}}\right)\frac{T}{\dot{Q}^\circ}$$

$$\boxed{\ln\left[f(X_{HL})\, \dot{Q}^\circ\right] = \ln\bar{A} + \ln T - \frac{\bar{B}}{T}}$$

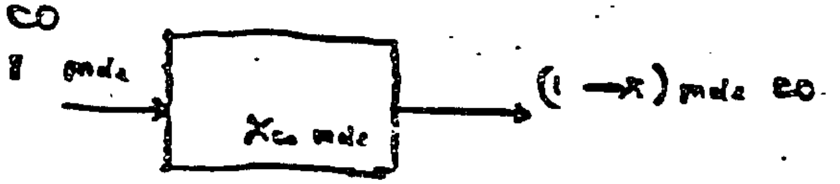
At least, two tests are needed at two different T's to get the two unknowns $\bar{A}$ & $\bar{B}$.

From Ⓐ & Ⓑ:

| To Find | Minimum # of Tests |
|---|---|
| k | 1. |
| Activation Energy | 2 at different T's |

7/20/92

## Estimation of $C_{CO_2}/C_{CO}$ ... plane 700B. Run 43



$$\boxed{X_{CO} \text{ mole CO}} \longrightarrow S_{CO_2} X_{CO} \text{ mole } CO_2$$

$S_{CO_2}$ CO₂ selectivity

$X_{CO}$ CO conversion

In this Run 43. $S_{CO_2} \approx 0.45$ ... ($\pm$ 0.025) ...

$$X_{CO} = 0.2 \sim 0.85$$

∴ In the out flow. (product)

$$\boxed{\frac{y_{CO_2}}{y_{CO}}} = \frac{X_{CO} \cdot S_{CO_2}}{1-X_{CO}} = \frac{0.09 \sim 0.38}{0.8 \sim 0.15} = 0.11 \sim 2.53$$

partial pr. ratio same molar ratio

we are putting less CO₂ than they are and less CO₂ might need less CO₂ interface membrane & why we get St. line

### Henry's Constant

By Nettelhoff et al (1985).

$$He_i = \frac{p_i}{c_i}$$

129

2/20/92 – ②

For CO. $He_{co} = 9.152\, e^{248/T}$ $\left(\frac{MPa\ \ell}{mol}\right)$

fugacity in unit

In our case $T = 265°C = 538\ K$

$$He_{co} = 9.152\, e^{248/538} = 14.51 \left(\frac{MPa \cdot \ell}{mol}\right)$$

For CO₂. $He_{co_2} = 24.64\, e^{-\frac{624.7}{T}}$ $\left(\frac{MPa \cdot \ell}{mol}\right)$

fugacity in unit

In our case $He_{co_2} = 24.64\, e^{-\frac{624.7}{538}} = 7.72$ $\left(\frac{MPa\ \ell}{mol}\right)$

$$\frac{C_{co_2}}{C_{co}} = \frac{P_{co_2}/He_{co_2}}{P_{co}/He_{co}} = \frac{P_{co_2}}{P_{co}}\,\frac{He_{co}}{He_{co_2}} = \frac{y_{co_2}}{y_{co}}\,\frac{He_{co}}{He_{co_2}}$$

$$\therefore \frac{C_{co_2}}{C_{co}} = (0.11 \sim 2.53)\,\frac{14.51}{7.72} = 0.21 \sim 4.76 \longleftarrow$$

Ledakowicz et al's case.

$T = 260°C$

$\frac{y_{co_2}}{y_{co}} = 0.78 \sim 4.21$ (from Table 2)

$\frac{C_{co_2}}{C_{co}} = 1.5 \sim 8.6$ (from Fig. 4)

$\therefore$ their $\frac{He_{co}}{He_{co_2}} = \frac{C_{co_2}/C_{co}}{y_{co_2}/y_{co}} = \frac{1.5 \sim 8.0}{0.78 \sim 4.21} \doteq 1.9 \longleftarrow$ very close to
the value used
in our case

2/25/92 — ③

Rate constant from Ledakowicz et al.

$$-r_{CO+H_2} = k \cdot \frac{C_{H_2}}{1 + 0.115 \frac{C_{CO_2}}{C_{CO}}}$$

Compared with 1st order case

$$-r_{CO+H_2} = b_1 \; C_{H_2}$$

We can define an "equivalent rate constant" $k_{eq}$

$$k_{eq} \equiv \frac{k}{1 + 0.115 \frac{C_{CO_2}}{C_{CO}}}$$

They gave.

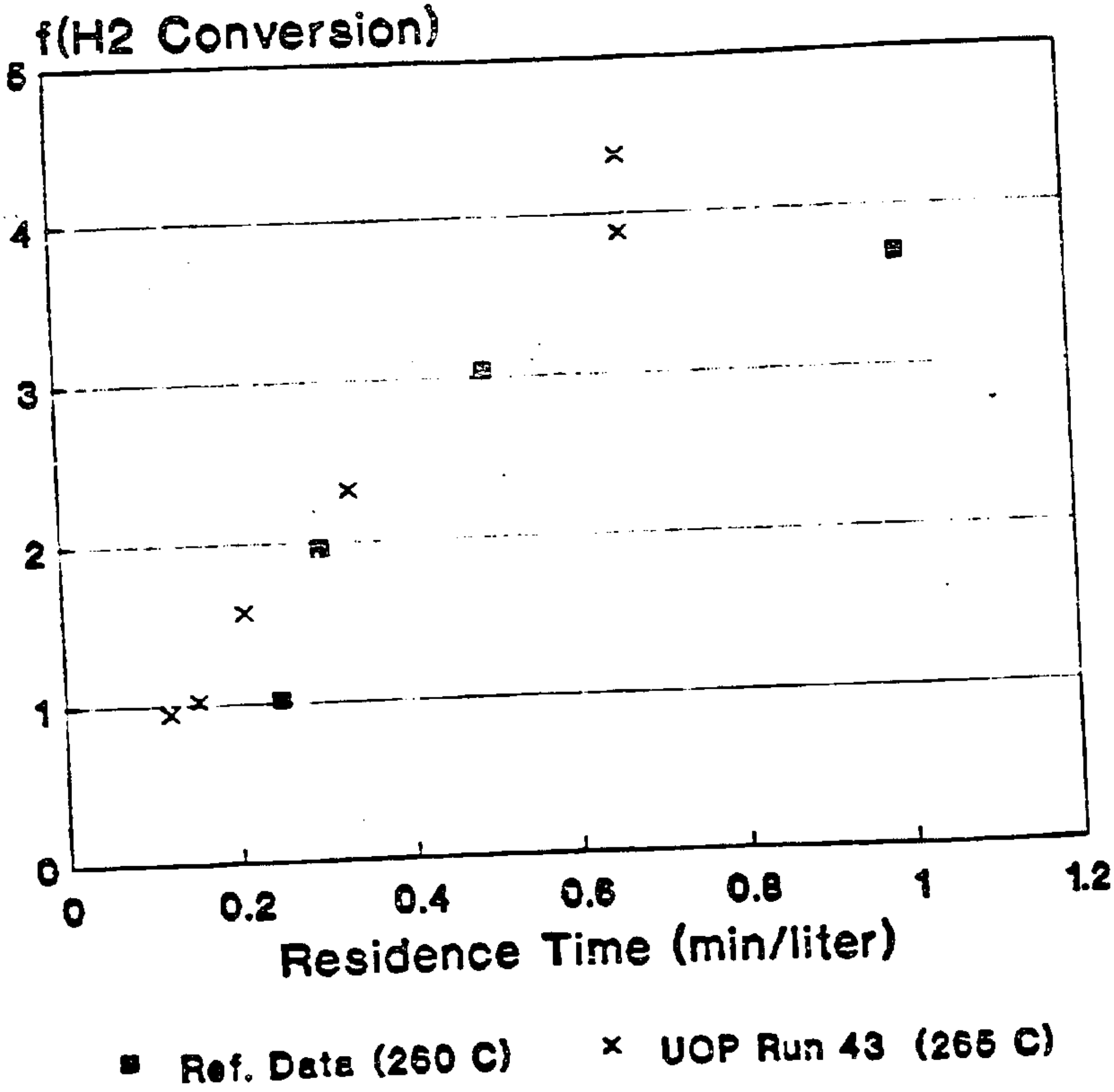
$$k_{eq} = \frac{1.8 \times 10^{10} \, e^{-\frac{12407}{T}}}{1 + 0.115 \frac{C_{CO_2}}{C_{CO}}}$$

In our case, $T = 538$ K. $\frac{C_{CO_2}}{C_{CO}} = 0.21 \sim 4.76$ then this gives:

$$k_{eq} = 0.87 \sim 1.32$$

Ours: $k_1 = 0.532$

# F-T CSTR MODEL TEST
# f(H2 Conv.) vs. Residence Time



Reference data taken from Ledakowicz
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