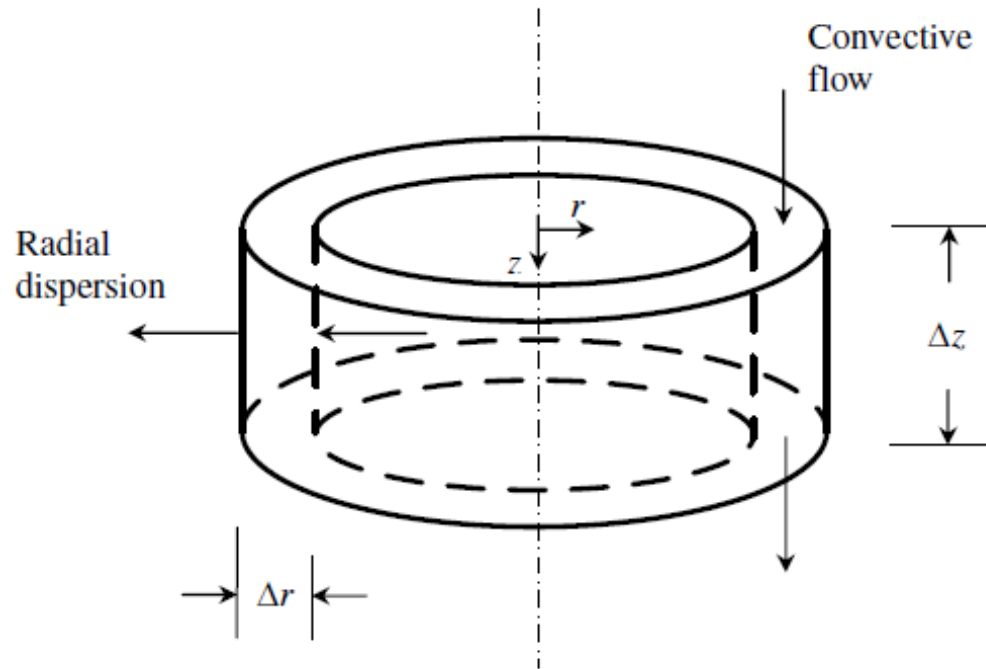


# CHE 611

# Advanced Chemical Reaction Engineering



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# Fitting of experimental data and discrimination among the various rate models

Now if the reaction is reversible, reversible kinetics are also included which is mostly true when high conversions are obtained during the experimentation. Therefore, using power law of the form including reversibility, it may be shown that

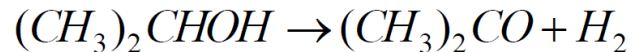
$$(-r) = k \cdot \left( p_A - \frac{p_B \cdot p_C^3}{K} \right)^n$$

Where  $K$  is reaction equilibrium constant. Only model is changed, the rest of the procedure of fitting the data is the same.

How many parameters are there,  
now, to be fitted?

# Activity

Acetone can be produced from isopropyl alcohol in a fixed bed reactor according to the following gas phase reaction

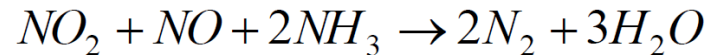
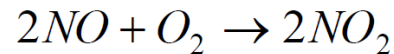


For each of the reactant species, find out the mole fraction relationship in terms of initial mole fractions and fractional conversion ( $X$ ) at any length in the reactor.

You may consider  $(CH_3)_2CHO = A$ ,  $(CH_3)_2CO = B$ , and  $H_2 = D$ .

# Activity

For the simultaneous gas phase reactions



for each of the reactant species, find out the mole fraction (at any length/time in the reactor) relation in terms of initial mole fraction and conversion or yield.

You may consider  $NO = A$ ,  $O_2 = B$ ,  $NO_2 = C$ ,  $NH_3 = D$ ,  $N_2 = E$ , and  $H_2O = F$ .

# Chemical equilibrium constant

$$\ln K = \frac{-\Delta G^\circ(T)}{R \cdot T}$$

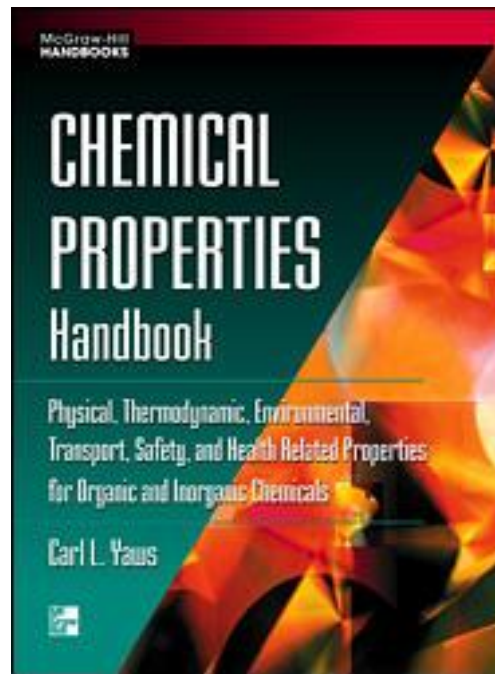
$$K = \exp\left(\frac{-\Delta G^\circ(T)}{R \cdot T}\right)$$

$$\Delta G^\circ(T) = -\sum \Delta G_i^\circ(T)$$

$G_i^\circ$  is a property of pure component  $i$  in its standard state at fixed pressure but depends on temperature.

# Determination of equilibrium constant

When experimental equilibrium constant is not available, one can find from the information of Gibbs' free energy of formation for each species. Please see Chemical Properties Handbook by Yaws [7].



# Chemical equilibrium constant

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**How one can calculate heat of reaction?**

# Chemical equilibrium constant

$$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^{\circ}}{R \cdot T^2}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$



# Experimental equilibrium constant of methylcyclohexane dehydrogenation

$$K_{\text{eq}} = K_{\text{eq}(T=650 \text{ K})} \cdot \exp \left[ -\Delta H_r^{\circ} / R \cdot (1/T - 1/650 \text{ K}) \right]$$

$$K = 3.60 \times 10^3 \cdot \exp \left( \frac{-217650}{R} \left( \frac{1}{T} - \frac{1}{650} \right) \right)$$

$K$  in  $\text{bar}^3$ ,  $R$  in  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , and  $T$  in  $\text{K}$

# Equilibrium composition for the example reaction

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Calculate the equilibrium composition of the reaction dehydrogenation of methylcyclohexane carrying out at 5 bar and 380 °C with 50 mol% H<sub>2</sub> in the feed.

# Equilibrium composition for the example reaction

$$K = \frac{p_{Tol} \times (p_{Hyd})^3}{p_{MCH}} = \frac{y_{Tol} \times (y_{Hyd})^3}{y_{MCH}} \times p^3$$

$$K = 3600 \cdot \exp\left(\frac{-217650}{R} \left(\frac{1}{T} - \frac{1}{650}\right)\right)$$

$K$  in  $\text{bar}^3$ ,  $R$  in  $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , and  $T$  in  $\text{K}$

# Mole fractions in the vapor phase (reaction mixture) at equilibrium conversion $X_{Ae}$

Component	Representation	Mole fraction
MCH	$A$	$\frac{y_{A0} \cdot (1 - X_{Ae})}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$
Tol	$B$	$\frac{y_{B0} + y_{A0} \cdot X_{Ae}}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$
H <sub>2</sub>	$C$	$\frac{y_{C0} + 3 \cdot y_{A0} \cdot X_{Ae}}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$
Inert	$I$	$\frac{y_{I0}}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$

# Equilibrium composition for the example reaction

$$K = \frac{p_{Tol} \times (p_{Hyd})^3}{p_{MCH}} = \frac{y_{Tol} \times (y_{Hyd})^3}{y_{MCH}} \times p^3$$

$$\frac{\left( \frac{(y_{B0} + X_{Ae} \cdot y_{A0})}{1} \right) \times \left( \frac{y_{C0} + 3 \cdot X_{Ae} \cdot y_{A0}}{1 + 3 \cdot X_{Ae} \cdot y_{A0}} \right)^3 \times p^3}{\left( \frac{(y_{A0} - X_{Ae} \cdot y_{A0})}{1} \right)} - K = 0$$

$$\frac{\left( \frac{(y_{B0} + X_{Ae} \cdot y_{A0})}{1} \right) \times \left( \frac{y_{C0} + 3 \cdot X_{Ae} \cdot y_{A0}}{1 + 3 \cdot X_{Ae} \cdot y_{A0}} \right)^3 \times p^3}{\left( \frac{(y_{A0} - X_{Ae} \cdot y_{A0})}{1} \right)} - 3600 \cdot \exp\left( \frac{-217650}{8.31434} \left( \frac{1}{T} - \frac{1}{650} \right) \right) = 0$$

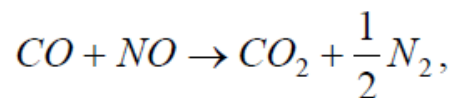
*Put p in bar and T in K.*

# Equilibrium composition for the example reaction: Excel spreadsheet (Solver application)

Ke =	2.32E+07	kPa <sup>3</sup>
Ke =	23.20752395	bar <sup>3</sup>
nMCHo =	0.99	mol/s
nH2o =	0.01	mol/s
yTol,0	0	
nN2o =	0	
T =	304.5	C
T =	577.65	K
p =	1.013	bar
f(Xe) =	-0.0000006577	= 0
Xe =	0.981659864	

# Homework problems

1. For the gas phase reaction

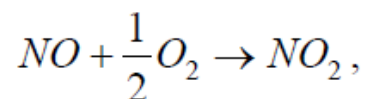


for each of the reactant species, find out the mole fraction (at any length/time in the reactor) relation in terms of initial mole fractions and fractional conversion ( $X$ ).

You may consider  $CO = A$ ,  $NO = B$ ,  $CO_2 = C$ , and  $N_2 = D$ .

Also write down the equilibrium constant in terms of equilibrium conversion and mole fractions of the reacting species.

2. For the gas phase reaction



for each of the reactant species, find out the mole fraction (at any length/time in the reactor) relation in terms of initial mole fractions and fractional conversion ( $X$ ).

You may consider  $NO = A$ ,  $O_2 = B$ , and  $NO_2 = C$ .

Also write down the equilibrium constant in terms of equilibrium conversion and mole fractions of the reacting species.

# Homework problems

3. Develop an expression for the equilibrium constant as a function of temperature applicable at low pressures for the dehydrogenation of cyclohexane (not methylcyclohexane). Use Gibbs energies of formation data from the book by Yaws (7, Yaws, C.L. 1999. Chemical properties handbook. McGraw-Hill).
4. Find out the equilibrium conversion for the reaction dehydrogenation of methylcyclohexane at 1.013 bar and temperatures of 550, 575, 600, 625, and 650 K. Use equation on slide 31 for equilibrium constant.
5. For the data given on slide 21 in a CSTR, find out the best fitting power law rate equation and also estimate the parameters involved. Fit the equations:
  - a) for conversion
  - b) for  $W/F_{A0}$For simplicity use only two equations, one for the irreversible reaction and the other including the reversibility as discussed in the class.



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