Chemical Reaction Engineering
Lecture 2: Review of Undergraduate Material

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Ethylene production by thermal cracking of ethane

➢ The thermal cracking of ethane is carried out in multitubular reactor. Typical production capacity of each tube is 10000 Tons per annum.

➢ Reactor specifications:

  ❑ Feed to the reactor: ethane + steam (?)

  ❑ Inlet pressure - 2.99 atm; temperature - 680°C

  ❑ Tube length 95 m, ethylene conversion – 60%

Cracking of ethane to ethylene

Reactor Design

Conversion
Volume
Production rate
CSTR +PFR
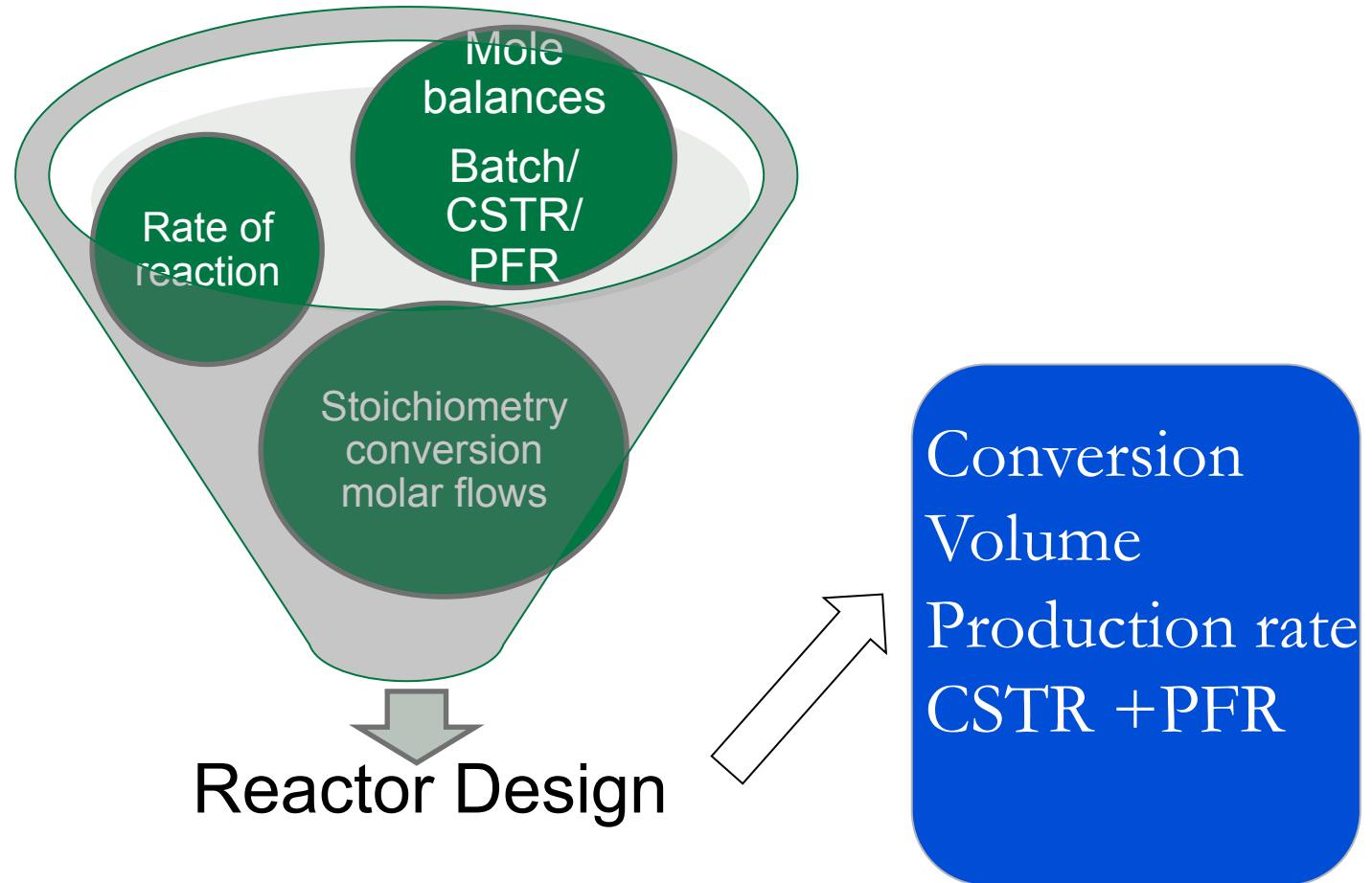
Topic 1: Basic concepts

➢ **Representation of reaction**

➢ **Extent of reaction and conversion**

➢ **Thermodynamics and chemical reactions**

  ❑ Heat of reaction

  ❑ Condition of equilibrium

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Representation of chemical reaction – single reaction

➢ Consider a single chemical reaction in N species A_1, A_2,…., A_N

➢ General representation:

$$\sum_{j=1}^{N} v_j A_j = 0$$

Representation of chemical reaction – multiple reactions

➢ Consider R chemical reactions in N species A_1, A_2,...., A_N

➢ General representation:

$$\sum_{j=1}^{N} v_{ij}A_j = 0, \quad i = 1, 2, ..., R$$

Representation of chemical reaction – independent reactions

➢ Stoichiometric matrix

$$\underline{\underline{v}} = \begin{pmatrix} v_{11} & \cdots & v_{1N} \\ \vdots & \ddots & \vdots \\ v_{R1} & \cdots & v_{RN} \end{pmatrix}$$

➢ Number of independent reaction

$$R = rank \left[\underline{\underline{v}} \right]$$

Progress of chemical reaction – single reaction

➢ Consider a reaction $\Sigma\ v_j A_j = 0$ taking place in a closed system

   n_{j0} = number of moles of species j present initially

   n_j = number of moles of species j at any time t

➢ Molar extent of reaction - α

$$\alpha = \frac{n_j - n_{j0}}{\nu_j}$$

Molar extent of reaction

$$\alpha = \frac{n_j - n_{j0}}{\nu_j}$$

➢ Properties of α

  ❑ defined for the reaction

$$\alpha = \frac{n_j - n_{j0}}{\nu_j} = \frac{n_k - n_{k0}}{\nu_k}$$

$$\Rightarrow \ n_k = n_{k0} + \frac{\nu_k}{\nu_j}\left(n_j - n_{j0}\right)$$

  ❑ Extensive property in moles

  ❑ Always positive

Conversion of species

➤ Conversion X

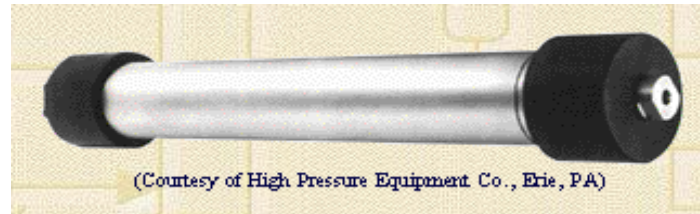$$X = \frac{n_{j0} - n_j}{n_{j0}}$$

➤ Stoichiometrically limiting species "k"
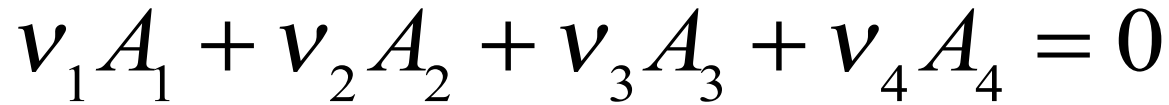
$$\min \left(-\frac{n_{j0}}{\nu_j} \right)$$

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Cracking of ethane to ethylene

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Molar flow at entry
Ethane, F_{10}

Molar flow at exit
Ethane, F_1
Ethylene, F_2 …

(Courtesy of High Pressure Equipment Co., Erie, PA)

Stoichiometric tables – Flow reactor

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

Species	Entry (mol/min)	Change (mol/min)	Exit from the reactor (mol/min)
A_1	F_{1O}	$-(F_{10}X)$	$F_1 = F_{10} - F_{10}X$
A_j j=2,3, 4	F_{jO}	$-\nu_j/\nu_1 (F_{10}X)$	$F_j = F_{j0} - \nu_j/\nu_1 F_{10}X$
I (inerts)	F_{I0}	-----	$F_I = F_{I0}$
Total	F_{T0}		$F_T = F_{T0} - (\Sigma \nu_j/\nu_1)F_{10}X$ $F_T = F_{T0} + \delta F_{10}X$

Concentrations in terms of conversion

$$Pv = Z F_T RT$$
$$P_0 v_0 = Z_0 F_{T0} RT_0$$
$$\left. \right\} v = v_0 \left(\frac{P_0}{P} \right) \left(\frac{Z}{Z_0} \right) \left(\frac{T}{T_0} \right) \left(\frac{F_T}{F_{T0}} \right)$$

$$F_T = F_{T0} + \delta F_{10} X$$

$$\frac{F_T}{F_{T0}} = 1 + \delta \frac{F_{10}}{F_{T0}} X = 1 + \delta y_{10} X = 1 + \varepsilon X$$

$$v = v_0 \left(\frac{P_0}{P} \right) \left(\frac{Z}{Z_0} \right) \left(\frac{T}{T_0} \right) \left(1 + \varepsilon X \right)$$

Concentrations in terms of conversion

$$C_{A0} = \frac{F_{A0}}{v_0}$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0} - F_{A0}X}{v}$$

$$C_A = C_{A0}\left(\frac{1-X}{1+\varepsilon X}\right)\left(\frac{P}{P_0}\right)\left(\frac{Z_0}{Z}\right)\left(\frac{T_0}{T_0}\right)$$

$$C_B = C_{A0}\left(\frac{\Theta_B - b/aX}{1+\varepsilon X}\right)\left(\frac{P}{P_0}\right)\left(\frac{Z_0}{Z}\right)\left(\frac{T_0}{T_0}\right)$$

Summary – Stoichiometry of reaction

➢ **Keywords & concepts**

❑ Stoichiometric coefficients

❑ Multiple reactions

❑ Set of independent reactions

❑ Extent of reaction

❑ Conversion

❑ Stoichiometric tables

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Chemical Reaction Engineering
Lecture 3: Review of Undergraduate Material

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Ethylene production by thermal cracking of ethane

➢ The thermal cracking of ethane is carried out in multitubular reactor. Typical production capacity of each tube is 10000 Tons per annum.

➢ Reactor specifications:

❑ Feed to the reactor: ethane + steam (?)

❑ Inlet pressure - 2.99 atm; temperature - 680°C

❑ Tube length 95 m, ethylene conversion – 60%

Thermodynamic considerations

- Equilibrium conversion
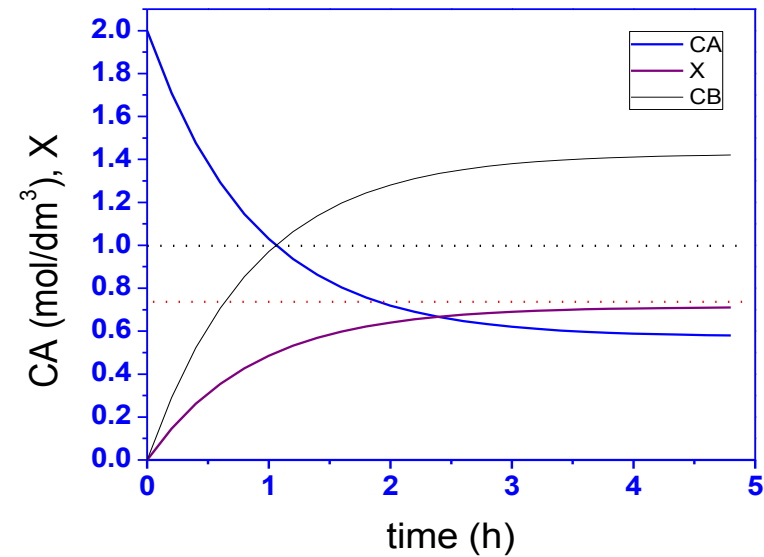
- Working conditions of the reactor
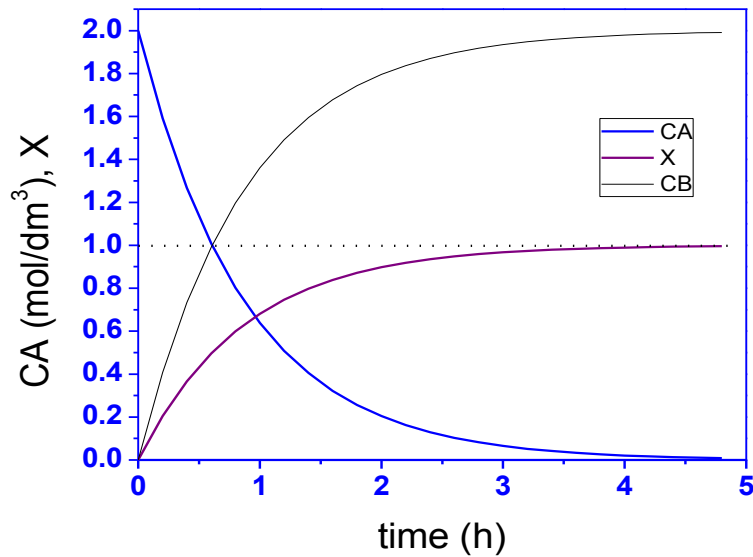
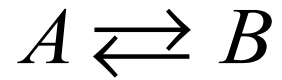- Heat effects in a chemical reaction
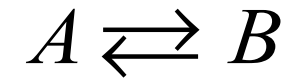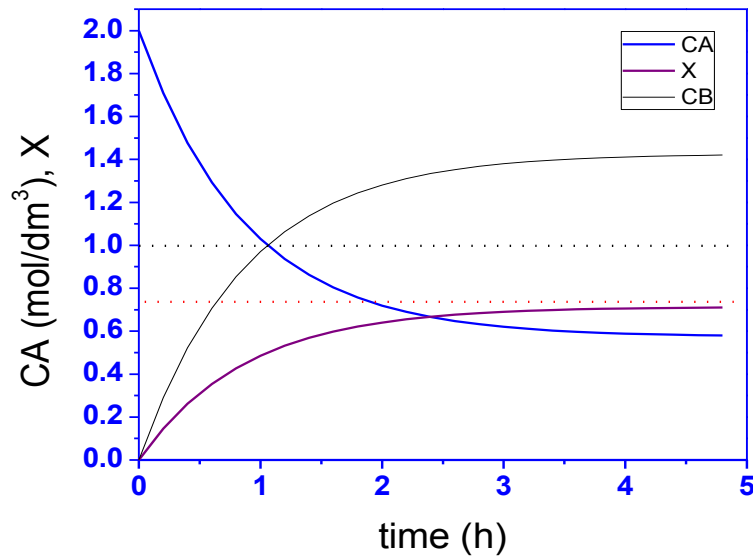
Why thermodynamics

$A \rightleftharpoons B$
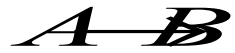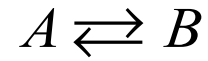
$$r = 2.6 \times 10^6 e^{-\left(\frac{15000}{T}\right)} C_A - 3.9 \times 10^{33} e^{-\left(\frac{25000}{T}\right)} C_B$$
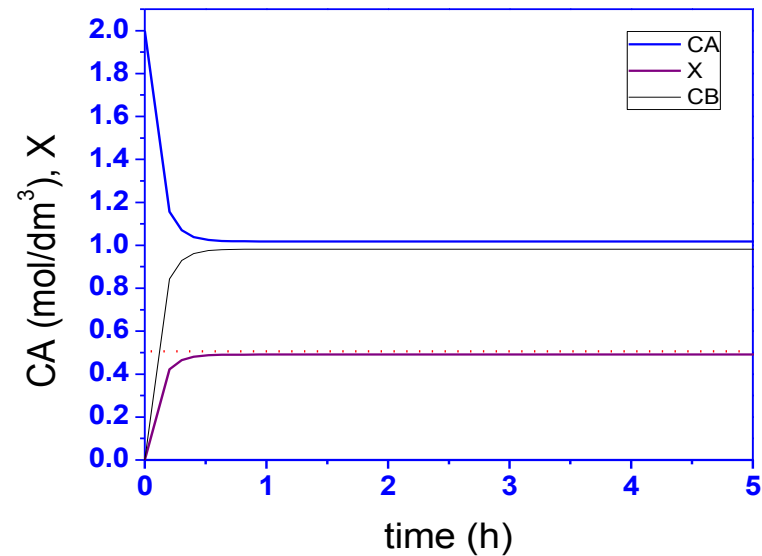
Effect of temperature

$$A \rightleftarrows B$$

$$T = 320$$

$$A \rightleftarrows B$$

$$T = 330$$

Chemical Equilibrium

➢ Consider a reaction $\Sigma\ v_j A_j = 0$ taking place at constant temperature T and pressure P. The system will spontaneously change in the direction of increasing entropy, reaching equilibrium when entropy can not increase further.

➢ Free energy and Gibb's equations

$$dG = Vdp - SdT + \sum_{j=1}^{N} \mu_j dn_j,$$

$$Chemical\ Potential\ \mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{T,P,n_k}$$

Chemical Equilibrium

$$Gibb's\ Equation \quad dG = Vdp - SdT + \sum_{j=1}^{N} \mu_j dn_j$$

$$Progress\ of\ reaction \quad n_j = n_{j0} + v_j \alpha \quad or \quad dn_j = v_j d\alpha$$

$$\Rightarrow \ dG = Vdp - SdT + \sum_{j=1}^{N} v_j \mu_j d\alpha$$

➢ Equilibrium condition

$$\left(\frac{\partial G}{\partial \alpha} \right)_{T,P} = \sum_{j=1}^{N} v_j \mu_j = 0$$

Chemical potential

➤ ## Perfect gas mixture

$$\mu_j\left(T,P,\underline{y}\right) = \mu_{j0}\left(T,P^r,\underline{y}^r\right) + RT\ln\frac{Py_j}{P^r}$$

➤ ## Non-ideal gas mixture

$$\mu_j\left(T,P,\underline{y}\right) = \mu_{j0}\left(T,P^r,\underline{y}^r\right) + RT\ln\frac{f_j}{f_j^r}$$

$\underline{y} = composition$,

$T = temperature$,

$P = pressure$

$superscript\ r = reference$

$P^r = 1\ atm$

$y^r = pure\ j$

$f_j = fugacity$

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Chemical potential

➤ Solution

$$\mu_j\left(T,P,\underline{x}\right) = \mu_{j0}\left(T,P^r,\underline{x}^r\right) + RT\ln\gamma_j x_j$$

$\underline{x} = composition$,

$T = temperature$,

$P = pressure$

$superscript\ r = reference$

$\gamma = activity\ coefficient$

Free energy change

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$\mu_j = \mu_{j0} + RT \ln\left(a_j\right)$$

$$\sum_{j=1}^{N} \nu_j \mu_j = \sum_j \nu_j \mu_{j0} + RT \sum_j \nu_j \ln\left(a_j\right)$$

$$\Delta G = \Delta G^0 + RT \ln\left(\prod_j a_j^{\nu_j}\right)$$

$$\Delta G = \Delta G^0 + RT \ln K_a$$

Equilibrium condition

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$\Delta G = \Delta G^0 + RT \ln\left(\prod_j a_j^{\nu_j} \right) = 0$$

$$\Delta G = \Delta G^0 + RT \ln K_a = 0$$

$$K_a = \left(\prod_j a_j^{\nu_j} \right) = \exp\left(\frac{-\Delta G^0}{RT} \right)$$

Equilibrium constant

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$K_a = \left(\prod_j a_j^{\nu_j} \right) = \exp\left(\frac{-\Delta G^0}{RT} \right)$$

Pressure $\quad K_P = \left(\prod_i P_j^{\nu_j} \right) = \left(\prod_i \left(Py_j \right)^{\nu_j} \right)$

Fugacity $\quad K_f = \left(\prod_i f_j^{\nu_j} \right)$

Concentration $\quad K_C = \left(\prod_i C_j^{\nu_j} \right)$

Equilibrium extent of reaction

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$K_P = \left(\prod_j P_j^{\nu_j} \right) \qquad\qquad P_j = y_j P = \frac{N_j}{N_T} P$$

$$N_j = N_{j0} + \nu_j \alpha$$

$$K_P = \left(\prod_j \left[P \frac{N_{j0} + \nu_j \alpha}{N_{T0} + \alpha \sum_j \nu_j} \right]^{\nu_j} \right) = F(\alpha)$$

Extent of reaction and operating conditions

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$K_P(T) = \left(\prod_j \left[P \frac{N_{j0} + \nu_j \alpha}{N_{T0} + \alpha \sum_j \nu_j} \right]^{\nu_j} \right) = F\left(\alpha, P, N_{j0} \right)$$

$$\frac{d}{dY}\left[\ln K_P(T) \right] = \frac{d}{dY}\left[F\left(\alpha, P, N_{j0} \right) \right] = \frac{\partial F}{\partial Y} + \frac{\partial F}{\partial \alpha} \frac{d\alpha}{dY}$$

Extent of reaction and operating conditions

$$v_1 A_1 + v_2 A_2 + v_3 A_3 + v_4 A_4 = 0$$

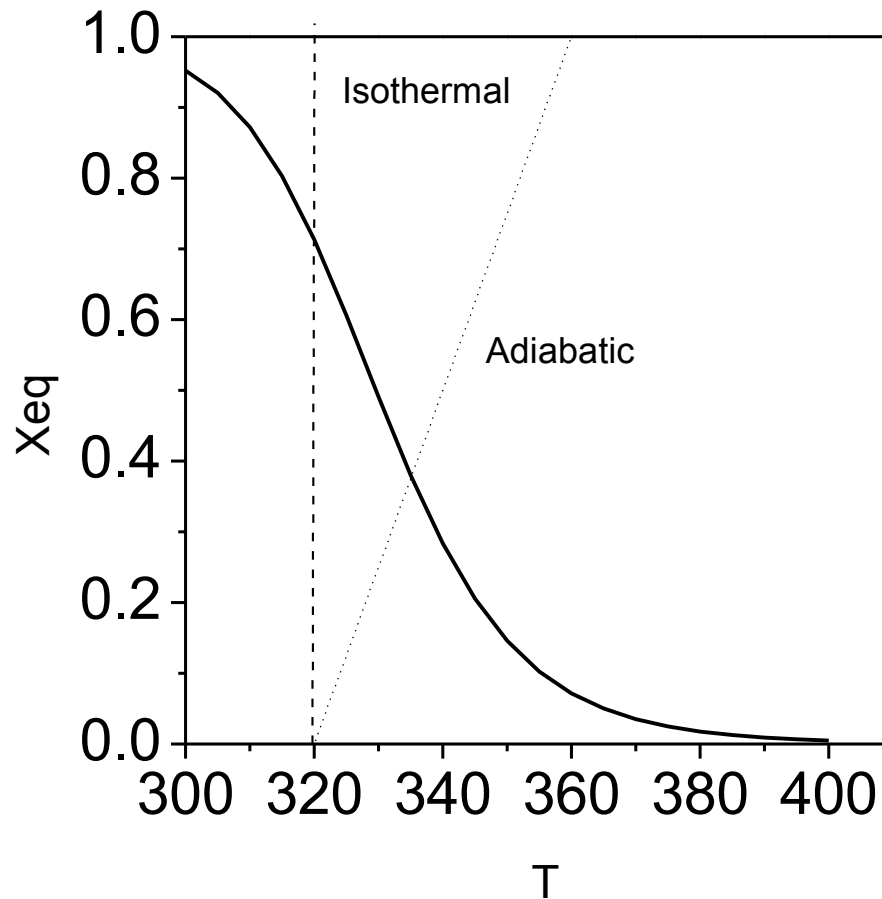$$\frac{d\alpha}{dY} = C \frac{F(\alpha)}{F'(\alpha)}$$

Temperature $\quad C = \dfrac{\Delta H}{RT^2} \qquad \Delta H = heat\ of\ reaction$

Pressure $\qquad C = -\dfrac{\displaystyle\sum_j v_j}{P} \qquad \displaystyle\sum_j v_j = change\ in\ no.\ of\ moles$

Inerts $\qquad C = ?$

Equilibrium conversion - Exothermic reaction

Equilibrium conversion - Endothermic reaction
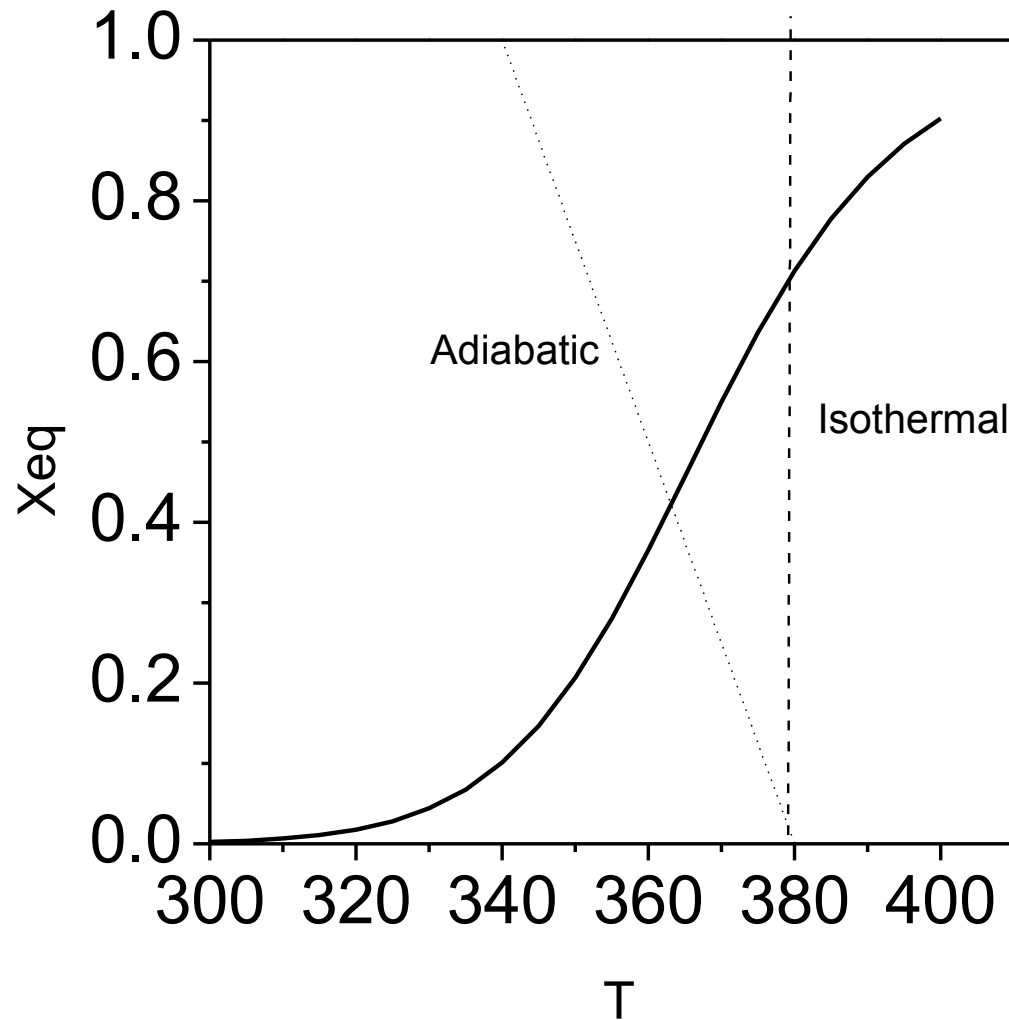
Equilibrium extent of reaction

$$\sum_{j=1}^{N} \nu_{ij} A_j = 0, \quad i = 1, 2, ..., R$$

$$K_{Pi} = \left(\prod_j P_j^{\nu_{ij}} \right)$$

$$N_j = N_{j0} + \sum_{i=1}^{R} \nu_{ij} \alpha_i$$

Heat of reaction

$$v_1 A_1 + v_2 A_2 + v_3 A_3 + v_4 A_4 = 0$$

$$\Delta H_R = \sum_j v_j h_j$$

$$h_j(T) = h_j^0 + \int_{298}^{T} C_{Pj}\, dT$$

$$\Delta H_R = \sum_j v_j h_j^0 + \sum_j v_j \int_{298}^{T} C_{Pj}\, dT$$

$$\Delta H_R = \Delta H_R^0 + \sum_j v_j \int_{298}^{T} C_{Pj}\, dT$$

Summary

➢ Free energy

➢ Chemical potential

➢ Condition of Equilibrium

➢ Equilibrium constant

➢ Equilibrium extent of reaction

➢ Operating conditions

Chemical Reaction Engineering
Lecture 4: Review of Undergraduate Material

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Chemical Kinetics: Basic concepts

- ➢ Kinetics of irreversible and reversible reactions
    - ❑ Power law kinetics
    - ❑ Law of mass action kinetics
- ➢ Rate of simple reactions

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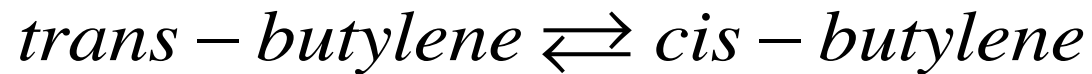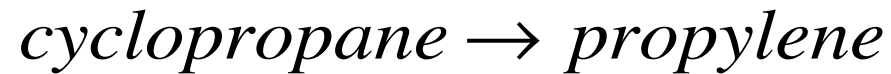
Classification of reactions

➢ **Based on mechanism of the reaction**

- ❑ Elementary and nonelementary reactions

Example: chlorination of nitric oxide to give nitrosyl chloride

$$2NO + Cl_2 \rightarrow 2NOCl$$
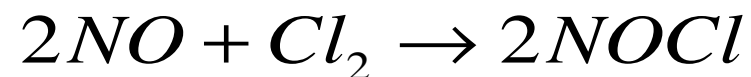
Classification of reactions

➢ Based on the direction of the reaction

  ❑ Irreversible and reversible reactions

$$cyclopropane \rightarrow propylene$$

$$trans-butylene \rightleftarrows cis-butylene$$

Classification of reactions

➢ Based on number of phases present in the system

 ❑ Homogenous and heterogeneous reactions

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

$$CO_2(g) + NaOH(l) \rightarrow NaHCO_3(l)$$
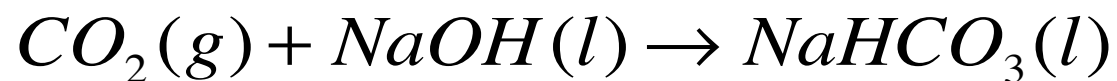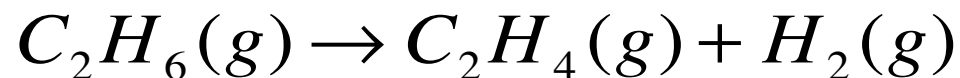
Rate of chemical reaction – single reaction

➤ Consider a reaction Σ $v_j A_j$ = 0 taking place in a closed, isothermal, constant pressure system

➤ Rate of reaction - r

$$r = \frac{1}{V}\frac{d\alpha}{dt} \qquad \alpha = \frac{n_j - n_{j0}}{v_j}$$

$$r_j = \frac{1}{V}\frac{dn_j}{dt}$$

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Reaction rate

➢ Consider a reaction Σ $v_j A_j$ = 0 taking place in a closed, isothermal, constant pressure system

$$r = r(T,P,y_1,y_2...y_{N-1})$$
$$= r(T,P,C_1,C_2...C_{N-1})$$
$$= r(T,C_1,C_2...C_{N-1},C_N)$$

Reaction rate – power law kinetics

➢ Consider a reaction $\Sigma\, v_j A_j = 0$ taking place in a closed, isothermal, constant pressure system

$$r = k C_1^{q_1} C_2^{q_2} .....C_N^{q_N} = k \prod_{j=1}^{N} C_j^{q_j}$$

q_j is the order of the reaction wrt species A_j

$q = \Sigma\, q_j$ is the overall order
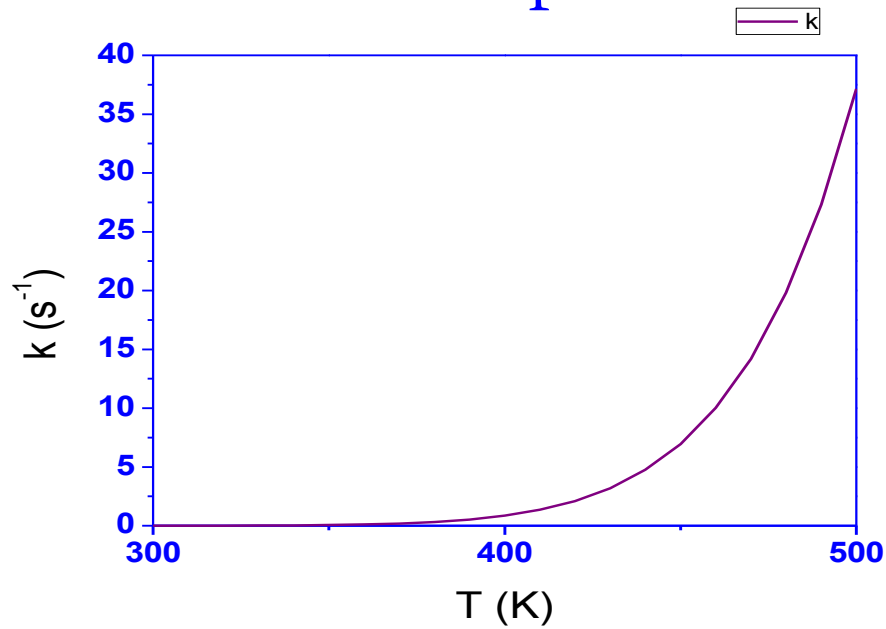
Reaction rate – law of mass action kinetics

➤ Consider a reaction $\Sigma\, v_j A_j = 0$ taking place in a closed, isothermal, constant pressure system
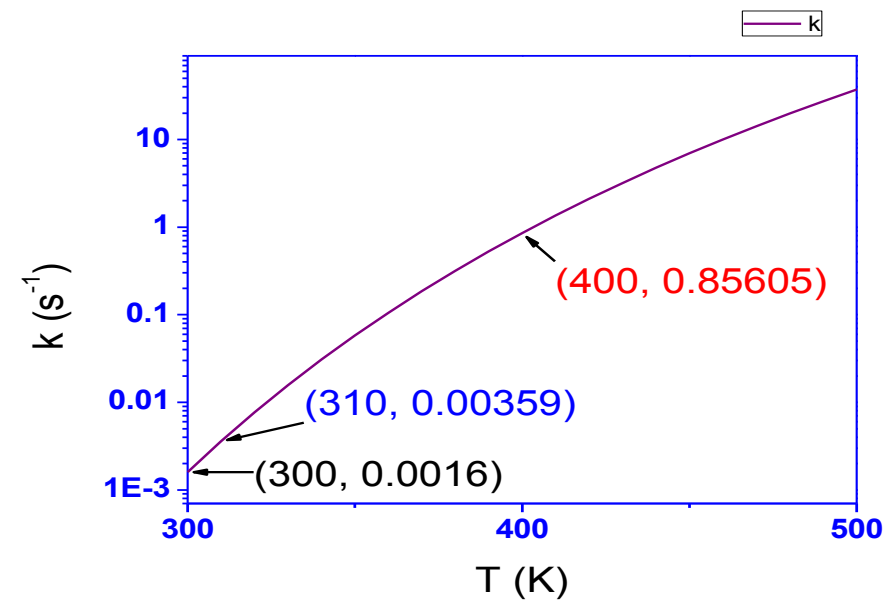
$$r = k \prod_{j=1}^{N} C_j^{q_j}$$

$$q_j = \frac{1}{2}\left(\left|v_j\right| - v_j\right)$$
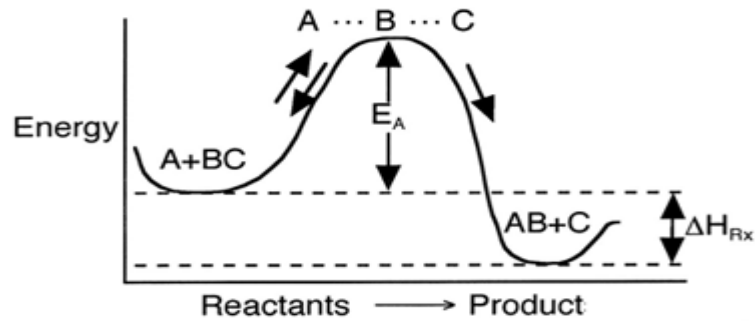
Effect of temperature on rate

$$k = Ae^{-\left(\frac{E}{RT}\right)}$$

Plot 1: k (s^{-1}) vs T (K), linear scale, rising from ~0 at 300 K to ~37 at 500 K.

Plot 2: k (s^{-1}) vs T (K), logarithmic scale, with labeled points (400, 0.85605), (310, 0.00359), (300, 0.0016).
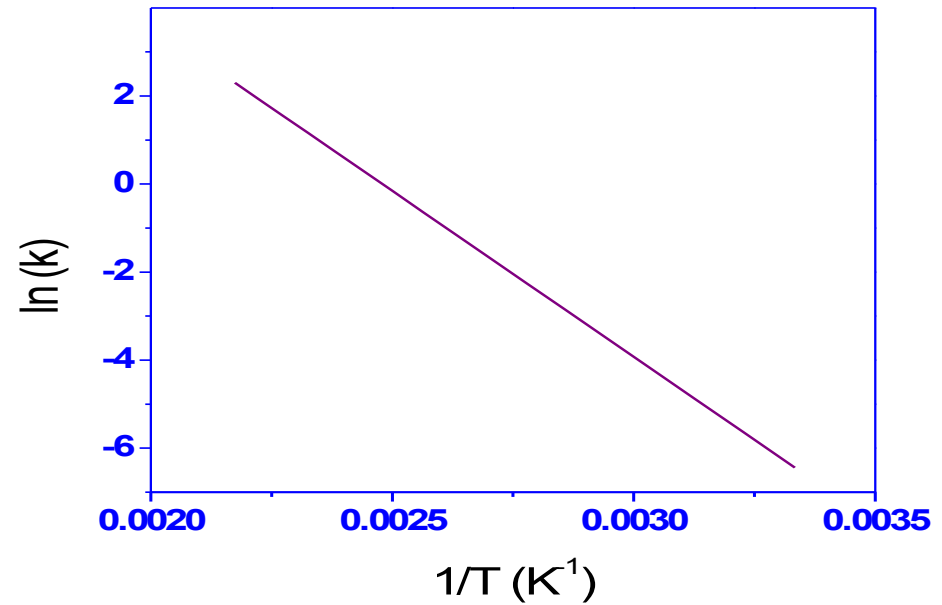
Activation energy

$$k = Ae^{-\left(\frac{E}{RT}\right)}$$

$$\ln k = \ln A - \frac{E}{RT}$$

Reaction rate – reversible reaction

➢ Consider a reaction Σ $v_j A_j$ = 0 taking place in a
  closed, isothermal, constant pressure system

$$r = k_f \prod_{j=1}^{N} C_j^{q_j} - k_b \prod_{j=1}^{N} C_j^{q_j'}$$

$$q_j = \frac{1}{2} \left(|v_j| - v_j \right)$$

$$q_j' = \frac{1}{2} \left(|v_j| + v_j \right)$$

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Variation of reaction rate with progress of reaction

➢ Consider a reaction $\Sigma\, v_j A_j = 0$ taking place in a
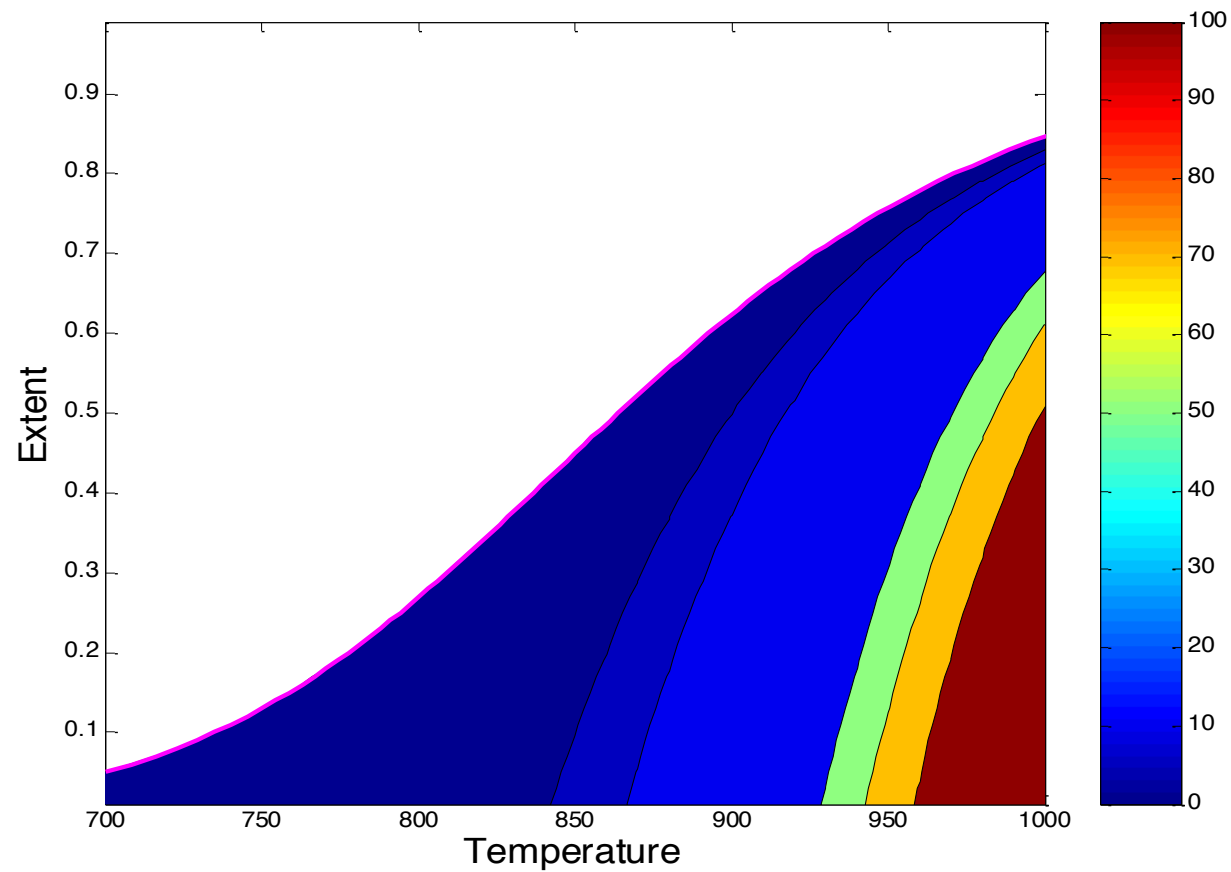closed, isothermal, constant pressure system

$$r = r_f - r_b = k_f(T)\prod_{j=1}^{N} C_j^{q_j} - k_b(T)\prod_{j=1}^{N} C_j^{q_j'}$$

$$C_j = C_{j0} + \alpha v_j$$

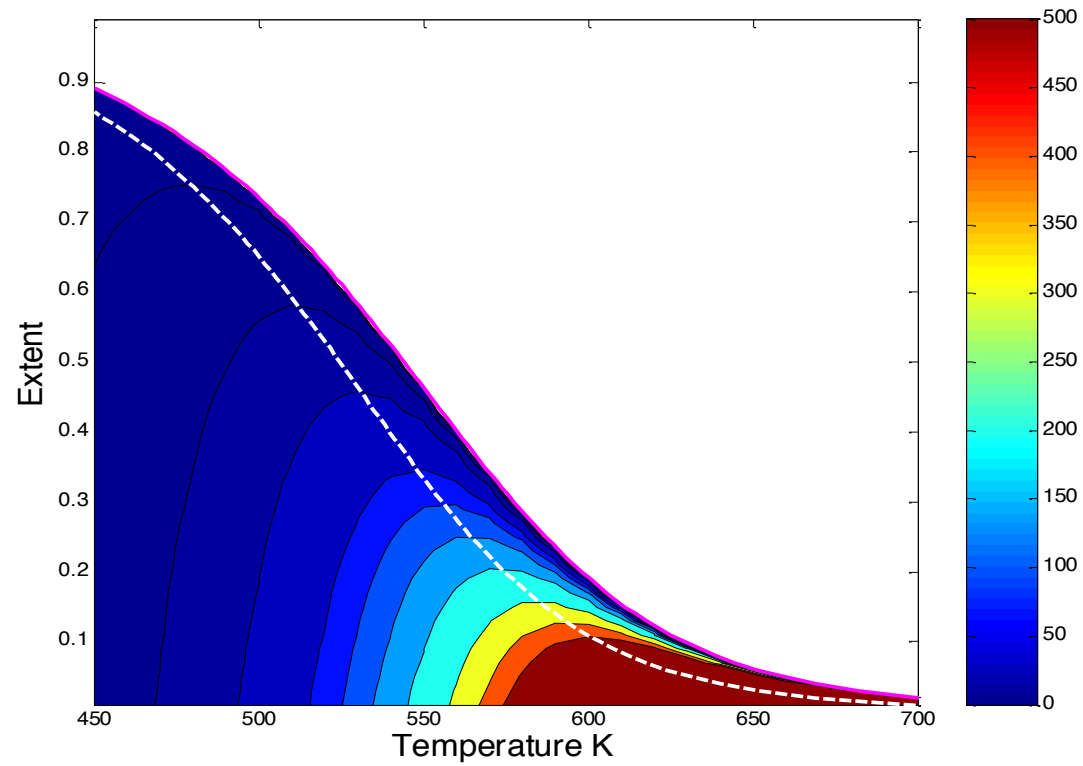$$r(\alpha, T) = r_f(\alpha, T) - r_b(\alpha, T)$$

Rate contours – endothermic reaction

Rate contours – exothermic reaction

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Summary

➢ Rate of reaction

➢ Power law kinetics

➢ Law of mass action kinetics

➢ Exothermic and endothermic reactions

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