1 Lecture 0: Intro to Reaction Engineering

1. Reaction engineering

   Understanding, modeling, designing, using, controlling, analyzing, improving anything in which chemical reactions happen.

1. Reaction engineering applications
   (a) Traditional
      i. Industrial chemical/petroleum processes
      ii. Fine chemical/pharmaceutical processes
      iii. Emerging, eg biorefinergy, shale gas, http://cistar.us
   (b) Energy storage, batteries, fuel cells
   (c) Environmental systems
      i. Atmosphere, lake, bioreactor (water purification), catalytic convertor
   (d) Biological systems
      i. Cell, organ, body
   (e) Laboratory reactors - interrogate, quantify
   (f) Research - improved materials (catalysts), improved processes, understand limitations
      i. Sabatier plot, https://doi.org/10.1038/nchem.121

2. Course structure
   (a) Quantifying chemical reactions
      i. Stoichiometry
      ii. Thermodynamics - heat flow, direction, equilibrium
      iii. Kinetics - rates, mechanisms
   (b) Physical/chemical interactions
      i. Transport, mixing, diffusion resistance, ...
   (c) Chemical reactors
      i. Ideal 0 and 1-dimensional
      ii. Non-ideal
      iii. Non-isothermal
      iv. Non-steady state
      v. Multiphase
   (d) Chemical processes (beyond us)
   (e) Markets (beyond us)

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2 Stoichiometry and reactions

1. Substances
2. Amounts
   (a) mass, moles, volumes
   (b) flow rates
3. compositions
   (a) amount/total amount
4. Reactions and stoichiometric coefficients
   (a) Advancements $n_j = \sum_i \nu_{ij}\xi_i$
   (b) Limiting reagents

3 Chemical thermodynamics and equilibria

1. Chemical reactions $\sum_j \nu_j A_j = 0$
2. Thermodynamic potential differences
   (a) Standard states
   (b) Formation reactions
   (c) Reaction enthalpy $\Delta H^\circ(T) = \sum_j {}_j H_j^\circ(T) = \sum_j \nu_j H_{f,j}^\circ(T)$
   (d) Reaction entropy $\Delta S^\circ(T) = \sum_j {}_j S_j^\circ(T)$
3. Equilibrium-closed system
   (a) Free energy vs reaction advancement, $G(\xi, T) = \sum_j n_j \mu_j = \sum_j (n_{j0} + \nu_j \xi)\left(\mu_j^\circ(T) + RT \ln a(\xi, T)\right)$
   (b) Equilibrium $(\partial G/\partial \xi)_{T,P} = 0$
   (c) Equilibrium constants and algebraic solutions
   (d) Multiple reactions
4. Le'Chatlier principle - system at equilibrium responds to oppose any perturbation
   (a) Pressure, composition
   (b) Temperature: Gibbs-Helmholtz and van't Hoff
5. Equilibrium-open system
   (a) Reaction phase diagrams, see http://pubs.acs.org/doi/abs/10.1021/jacs.6b02651 for an example
   (b) Electrochemical reactions
6. The molecular interpretation
7. Non-ideal activities
8. Surface adsorption
   (a) Langmuir

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4 Empirical kinetics

1. rates
2. reactor mass balance
3. rate expressions
4. rate orders
5. apparent orders
6. integrated rate expressions
7. temperature and Arrhenius expression
8. analyzing reactor data

5 Molecular basis

1. reaction pathway, detailed balance
2. bimolecular, collision theory, TST
3. unimolecular reactions

6 Mechanisms

1. QSSA
2. Pre-equilibrium

7 Heterogeneous reactions

1. adsorption, L-H
2. TPD
3. catalysis
4. Sabatier analysis

8 Liquid-phase reactions

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Table 1: Equilibrium and Rate Constants

Equilibrium Constants $a\ \mathrm{A} + b\ \mathrm{B} \rightleftharpoons c\ \mathrm{C} + d\ \mathrm{D}$

$$
\begin{aligned}
K_{eq}(T) &= e^{\Delta S^\circ(T,V)/k_B} e^{-\Delta H^\circ(T,V)/k_B T} \\
K_c(T) &= \left(\frac{1}{c^\circ}\right)^{\nu_c+\nu_d-\nu_a-\nu_b} \frac{(q_c/V)^{\nu_c}(q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a}(q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta} \\
K_p(T) &= \left(\frac{k_B T}{P^\circ}\right)^{\nu_c+\nu_d-\nu_a-\nu_b} \frac{(q_c/V)^{\nu_c}(q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a}(q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}
\end{aligned}
$$

Unimolecular Reaction $[A] \rightleftharpoons [\mathrm{A}]^\ddagger \rightarrow C$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{\bar{q}_\ddagger(T)/V}{q_A(T)/V} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + k_B T \quad A = e^1 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

Bimolecular Reaction $\mathrm{A} + \mathrm{B} \rightleftharpoons [\mathrm{AB}]^\ddagger \rightarrow \mathrm{C}$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{q_\ddagger(T)/V}{(q_A(T)/V)(q_B(T)/V)} \left(\frac{1}{c^\circ}\right)^{-1} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + 2k_B T \quad A = e^2 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

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