ChE 641 | Lecture 31

Condensed Phase Reactions

- Evaporation
- Devolatilization
- Char Reaction
- Energy Equation
- Potential Problems

Particle Continuity Equation

$$\frac{d\alpha_p}{dt} = r_p$$

→ Simple, but effective.

→ Need to know net rate of reaction

$$r_p = \sum_n r_n$$

What different kinds of reaction are possible?

A. Evaporation (droplets or moist particles)

B. Devolatilization (chemical transformation & vaporization)

C. Heterogeneous oxidation

A. Evaporation: Where do we start?

Raoult's Law for children: $X_i P_i^v = y_i P_{tot}$

This is the driving force. Define the system at the surface of the particle/droplet

$X_i = 1$ for pure liquid

$$y_i = \left.\frac{P_i^v}{P_{tot}}\right|_{T_{surf}}$$

skip in '98

If we know P_i^v at one T, Claussius Clapeyron Equ. says

$$\frac{d \ln P^v}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

If $\Delta H_{vap} \equiv$ constant, then $\ln \frac{P^v(T_2)}{P^v(T_1)} = \frac{\Delta H_v}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

If we know $y_i|_{surface}$, how do we get the evaporation rate?

A. Boiling (limited by heat transfer)

$$r_w = \frac{\text{heat transfer rate}}{\Delta H_v} = \frac{J/s}{J/kg} = kg/s$$

B. Non-Boiling (This is what really happens)

from BS;L (21.1-13)

mass fraction in gas phase

$$r_w = k_w (x_{i,s} - x_{i,b}) + x_{i,s} r_{tot}$$

mass transfer coefficient

$$r_w = k_w (x_{i,s} - x_{i,b}) + x_{i,s} r_w + x_{is} \Sigma r_{other}$$

$$(1 - x_{is}) r_w = k_w (x_{i,s} - x_{i,b}) + x_{i,s} \Sigma r_{other}$$

$$r_w = \frac{k_w (x_{i,s} - x_{i,b}) + x_{i,s} \Sigma r_{other}}{1 - x_{i,s}}$$

→ k_w from Sherwood number (mass transfer correlation), adjusted for high mass transfer rates

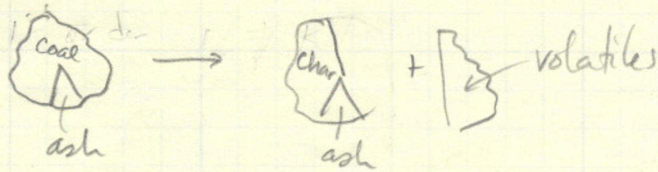
$$Sh = \frac{k_w d_p}{\mathcal{D}} = 2 + .5 Re^{1/2} Sc^{1/3} \cong 2 \text{ for small particles}$$

$$k_w = \frac{2 Sh \mathcal{D}}{d_p}$$

adjusting for high mass transfer, $k_w = \frac{2 Sh \mathcal{D}}{d_p} \left[\frac{B_{tot}}{(e^{B_{tot}} - 1)} \right]$

B. Devolatilization rate

Beginners



$\alpha_{coal} \rightarrow \alpha_{char} + \alpha_{vol}$

1-step

Smith & Smoot 3.1

$$r_V = k_V \, (V^{\infty} - V)$$

$\uparrow$ pre-specified volatile yield

2-step model

Smith & Smoot 3.4

$$\text{Coal} \begin{cases} \xrightarrow{k_1} Y_1\,(\text{vol}) + (1-Y_1)\,\text{char} \\ \xrightarrow{k_2} Y_2\,(\text{vol}) + (1-Y_2)\,\text{char} \end{cases}$$

competing reactions

Distributed

Smith & Smoot 3.7

$$\frac{V_\infty - V}{V_\infty} = \int_0^\infty \left[e^{-\int_0^t k\,dt} \right] \frac{1}{\sigma\sqrt{2\pi}} \, e^{-\frac{(E-E_0)^2}{2\sigma^2}} \, dE$$

→ need E_0, σ, k_0

→ need to keep track of bins for integral (Gaussian quadrature)
(like integrating several particles with different E's, then weighting them)

Devolatilization

What really happens

- chemical structure — better input data on coal structure
- break bonds between clusters — bond-breaking rate
- form light gas
- form liquids

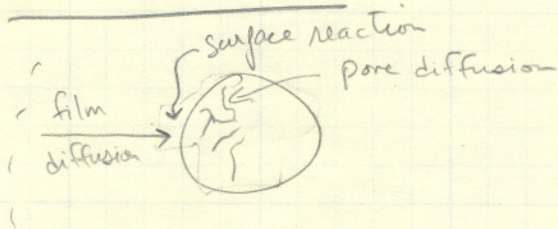
} need molecular weights

- liquids evaporate — need vapor pressure and multi-component Raoult's law (Flash calculation)
- mass transfer (usually high → adjust k_{mass} ; h_{heat} through θ factor)
- swelling / density change

⇓

CPD

Char Oxidation



- pore diffusion incorporated into "apparent" reactivity
- pseudo-steady state assumed (solve for $P_{ox,surf}$)

film diffusion = surface reaction

Example: For first order,

$$r_{char} = \overset{\text{@ film T}}{k_m}\left(\underset{\text{at gas T}}{P_{O_2,b}} - P_{O_2,s}\right) = \overset{\text{at Particle T}}{k_{surf}}\, P_{O_2,s}$$

Solve for $P_{O_2,s}$, then calculate r_{char}

Complications

① simultaneous reactions { evap. / devol. / char ox. { multiple oxidizers

② effects of high mass transfer

→ film diffusion limit $\quad r_{char} = k_m\left(P_{O_2,b} - \cancel{P_{O_2,s}}^{\,0}\right)$

→ effects on heat & mass transfer coefficients

Warning

Make sure you reconcile units! $\quad \dot{r}_C = \frac{kg\text{-}C}{cm^2\, s}$

$\dot{r}_{O_2} = \frac{kg\text{-}O_2}{cm^2\, s}$

also - molar rates sometimes reported

PCGC-3 (for 1st order only)

$$r_{hjl} = \frac{A_j^2 M_{hj} M_g \phi_l k_{cjl} k_{jl} \zeta_j C_{olg} C_g}{M_g A_j C_g(\zeta_j \underset{\uparrow}{k_{jl}} + \underset{\uparrow}{k_{cjl}}) + \underset{\uparrow}{r_j}}$$

kinetic coefficient $\quad$ mass transfer $\quad$ total reaction rate

Energy Equation

$$\frac{d(\alpha_p h_p)}{dt} = Q_{conv} + Q_{rad} + r_p h_{pag}$$

enthalpy of gaseous products leaving coal

blowing

$$Q_c = \theta h A (T_g - T_p)$$

$$Nu = \frac{hd}{k_{g,film}} = 2 + .65 Re_p^{.5} Pr^{1/3}$$

$$\theta = \frac{B}{e^B - 1}$$

Q_r = net radiation to particle

complicated → { particle-particle, gas-particle, wall-particle }

Alternate form, which is equivalent but not used

$$m_p C_p \frac{dT_p}{dt} = h A_p (T_g - T_p) \frac{B}{e^B - 1} + \underbrace{\sigma \epsilon_p A_p (T_w^4 - T_p^4)}_{Q_r \text{ for simple system}} - \sum_n \frac{dm_n}{dt} \Delta H_{rxn,n}$$

– so we have momentum, continuity $\left\{\begin{matrix}\text{moisture}\\ \text{coal}\\ \text{(char)}\end{matrix}\right\}$, & energy

Each as form

$$\frac{dy}{dt} = f(y, \text{other variables})$$

→ use Runge-Kutta, etc.

PCGC-3

$$\frac{dy}{dt} = a(y_0 - y) + s$$

Integrate once analytically from t_1 to t_2

$$\ln\left[\frac{a(y_0 - y_{t_2}) + s}{a(y_0 - y_{t_1}) + s}\right] = -a\Delta t$$

This works well for equation of motion (Lagrangian trajectories)

$$a = \frac{C_D Re}{24 t_j}$$

$$s = \pm g$$