Method of Moments.

$n = n(m)$: $\frac{\#}{m^3 \cdot kg}$.

- $$\frac{\partial n}{\partial t} + \nabla \cdot (\vec{V} n) + \nabla \cdot (\vec{V}_T n) = \dot{N} + \dot{G} + \dot{C}$$

- $$M_k = \int_0^\infty m^k n(m)\, dm$$

- $$V_T = -0.556\, \nu \frac{\nabla T}{T}$$

- $$\frac{\partial M_k}{\partial t} + \nabla \cdot (\vec{V} M_k) + \nabla \cdot (\vec{V}_T M_k) = \underbrace{\int m^k \dot{N}\, dm}_{\dot{N}_k} + \underbrace{\int m^k \dot{G}\, dm}_{\dot{G}_k} + \underbrace{\int m^k \dot{C}\, dm}_{\dot{C}_d}$$

$(=)$ $\frac{kg^k}{m^3 \cdot s}$

Nucleation.

$$\dot{N} = J_{nuc} \cdot \delta(m - m_{nuc})$$

$$J_{nuc} \; (=) \; \frac{\#}{m^3 \cdot s}$$

$$\delta \; (=) \; \frac{1}{kg} \qquad \text{So that } \int \delta(m - m_{nuc})\, dm = 1$$

Example: for $C_2H_2 \longrightarrow 2\,C(s) + H_2$

$$R_{nuc} = 0.1 \times 10^5\, e^{-21100/T}\, [C_2H_2] \quad (=) \; \frac{kmol}{m^3 \cdot s}$$

$$J_{nuc} = \frac{2\, N_a R_{nuc}}{C_{min}} \; ; \qquad C_{min} \; (=) \; \frac{\#\ \text{Carbons}}{\text{nucleus}}$$

$$\underbrace{\int m^k \dot{N}\, dm}_{} = \int_0^\infty m^k J_{nuc}\, \delta(m - m_{nuc})\, dm$$

$$\boxed{\dot{N}_k = m_{nuc}^k J_{nuc}}$$

Growth.

$$\dot{G} = \frac{\partial}{\partial m}\left(V_g \cdot n\right) \quad (=) \quad \frac{\#}{m^3 \cdot s \cdot kg}$$

$$= \frac{1}{\cancel{kg}} \frac{\cancel{kg}}{s} \cdot \frac{\#}{m^3 \cdot kg}$$

V_g (=) kg/s

$$V_g = k_s \cdot S(m)$$

$$k_s = \frac{kg}{m^2 \cdot s}$$

$$S(m) = \frac{m^2}{\text{Particle}}.$$

V_g follows from: $\dot{G} = \lim\limits_{\Delta m \to 0} \frac{k_s}{\Delta m}\left(n_{i-1} S_{i-1} - n_i S_i\right)$,

- where Δm is the spacing bet. particles
- we grow particle i from $i-1$ and we lose particle i as it grows.

$$\dot{G}_k = \int_0^\infty m^k \frac{\partial}{\partial m}\left(V_g n\right) dm \qquad \int_0^\infty u\,dv = uv\Big|_0^\infty - \int_0^\infty v\,du$$

let $u = m^k \rightarrow du = k m^{k-1} dm$

$dv = \frac{\partial}{\partial m}\left(V_g n\right) dm \rightarrow v = V_g n$

$$= \cancelto{0}{m^k V_g n\Big|_0^\infty} - \int_0^\infty V_g n\, k m^{k-1} dm$$

$$\boxed{\dot{G}_k = -k \int_0^\infty V_g m^{k-1} n\, dm} \Longrightarrow \text{in terms of } M \text{ not } V_g \Longrightarrow$$

$$V_g = k_s S(m)$$

$$\left.\begin{aligned} S &= \pi d^2 \\ m &= \rho_s \frac{\pi}{6} d^3 \end{aligned}\right\} \longrightarrow d = \left(\frac{6m}{\rho_s \pi}\right)^{1/3} = \left(\frac{6}{\rho_s \pi}\right)^{1/3} m^{1/3}$$

$$\rightarrow S = \pi \left(\frac{6}{\pi \rho_s}\right)^{2/3} m^{2/3}$$

$$\underline{\underline{V_g = k_s \cdot \pi \left(\frac{6}{\pi \rho_s}\right)^{2/3} m^{2/3}}} \rightsquigarrow \dot{G}_k = -k \int_0^\infty V_g \, m^{k-1} n \, dm$$

$$\boxed{\dot{G}_k = -k_s \pi \left(\frac{6}{\pi \rho_s}\right)^{2/3} k \, M_{k-1/3}}$$

Coagulation

$$\dot{C} = \frac{1}{2}\int_0^m \beta(\mu, m-\mu)\, n(\mu)\, n(m-\mu)\, d\mu - \int_0^\infty \beta(m,\mu)\, n(\mu)\, n(m)\, d\mu$$

$$\dot{C}_k = \int_0^\infty m^k \dot{C}\, dm$$

$$\dot{C}_k = \frac{1}{2}\int_0^\infty m^k \left[\int_0^m \beta(\mu, m-\mu)\, n(\mu)\, n(m-\mu)\, d\mu\right] dm - \int_0^\infty m^k \left[\int_0^\infty \beta(m,\mu)\, n(\mu)\, n(m)\, d\mu\right] dm$$

$\boxed{}$ (see back)

$$\dot{C}_k = \frac{1}{2}\int_0^\infty \left[\underbrace{\int_\mu^\infty m^k \beta(\mu, m-\mu)\, n(m-\mu)\, dm}\right] n(\mu)\, d\mu - \int_0^\infty\int_0^\infty \beta(m,\mu)\, m^k n(\mu)\, n(m)\, d\mu\, dm$$

let $u = m - \mu$

$\rightarrow du = dm$ (μ is const in inner integral)

for limits: $m = \mu \rightarrow u = 0$

$m = \infty \rightarrow u = \infty - \mu = \infty$

$$\dot{C}_k = \frac{1}{2}\int_0^\infty \left[\int_0^\infty (u+\mu)^k \beta(\mu, u)\, n(u)\, du\right] n(\mu)\, d\mu - (\text{term.})$$

- u is notational, so replace it with m

$$\dot{C}_k = \frac{1}{2}\int_0^\infty\int_0^\infty \beta(\mu, m)\, n(m)\, n(\mu) \left[(m+\mu)^k - 2m^k\right] dm\, d\mu$$

- where we've absorbed the second term
- Note: $(m+\mu)^k = \sum_{j=0}^{k} \binom{k}{j} m^j \mu^{k-j}$; $\binom{k}{j} = \frac{k!}{j!(k-j)!}$

$$\boxed{\dot{C}_k = \frac{1}{2}\int_0^\infty\int_0^\infty \beta(m,\mu)\, n(m)\, n(\mu) \left[-2m^k + \sum_{j=0}^{k} \binom{k}{j} m^j \mu^{k-j}\right] dm\, d\mu}$$

2 regimes:

Continuum: $\beta(m,\mu) = K_c\left(\frac{C(m)}{m^{1/3}} + \frac{C(\mu)}{\mu^{1/3}}\right)(m^{1/3} + \mu^{1/3})$

$$K_c = \frac{2k_BT}{3\mu}$$

$$C = 1 + 1.257 K_n$$

$$K_n = \frac{2\lambda}{d_p}$$

λ = mean free path.

$$\lambda = \nu\left(\frac{\pi M}{2RT}\right)^{1/2}$$

Free molecular:

$$\beta(m,\mu) = K_f\left[\frac{1}{m} + \frac{1}{\mu}\right]^{1/2}(m^{1/3} + \mu^{1/3})^2$$

$$K_f = \epsilon\sqrt{\frac{6k_BT}{\rho_s}}\left(\frac{3}{4\pi\rho_s}\right)^{1/6}$$

ϵ is a Van Der Walls enhancement factor.
$= 2.2$ in Kazakov 1998.

Transition: $\dot{C}_k = \frac{\dot{C}_{k,FM} \cdot \dot{C}_{k,cont}}{\dot{C}_{k,FM} + \dot{C}_{k,cont}}$: Harmonic mean.

Nucleation rates. – C_2H_2

$$C_2H_2 \Longrightarrow 2\,C(s) + H_2$$

- Leung et al 1991.

$$R = k\,[C_2H_2] \quad (=) \quad \frac{kmol}{m^3 \cdot s}$$

$$R = \underbrace{0.1\times10^5\, e^{-21100/T}}_{k\ (=)\ \frac{1}{s}}\ \underbrace{[C_2H_2]}_{kmol/m^3}$$

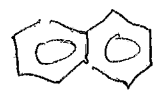
- "Results insensitive to C_{min} Given nuc size 1-10nm"
- $C_{min} = 100 \rightarrow 1.24$ nm

$$R_{nuc} = \frac{R \cdot 2 N_A}{C_{min}} \quad (=) \quad \frac{\#}{m^3 \cdot s} = \underbrace{\frac{kmol\ C_2H_2}{m^3 \cdot s}}_{R} \underbrace{\frac{2\ \cancel{kmol\ C}}{\cancel{kmol\ C_2H_2}}}_{2} \cdot \underbrace{\frac{\cancel{\#C}}{\cancel{kmol\ C}}}_{N_A} \cdot \underbrace{\frac{\#\ part}{\cancel{\#C}}}_{\frac{1}{C_{min}}}$$

$C_{min} = 100$

* • Lindstedt 2005 PCI 30 775

$$R_{nuc} = \frac{2 N_A}{C_{min}} \cdot 0.63\times10^4 e^{-21000/T} [C_2H_2]$$

$C_{min} = 10$ = Naphthalene, =  $= C_{10}H_8$

- Mehta 2009 PCI Gives above 2 references for nucleation.
- Bockhorn 1994: Lindstedt p 417 (424)
  - $C_{min} = 60$ $\rightarrow 1.0$ nm • Again, "results insensitive to C_{min} for size < 10nm"
  - The rate in Lind. 2005 (0.63×10^4) appears, but there is probably a typo in the eqns: See Table 27.2

Growth – C_2H_2

$$C_2H_2 \longrightarrow 2C_s + H_2$$

- Leung et al. 1991

$$\underbrace{R}_{} = \underbrace{k}_{\frac{m^{3/2}}{m \cdot s}} \underbrace{f(A)}_{\left(\frac{m^2}{m^3}\right)^{1/2}} \underbrace{[C_2H_2]}_{kmol/m^3} \quad (=) \quad \frac{kmol}{m^3 \cdot s}$$

$$R = 0.6 \times 10^4 e^{-12100/T} \cdot \sqrt{A}\ [C_2H_2]$$

$$A = m^2/m^3$$

- use $\sqrt{A}$ to account for reduced reactivity as soot ages.

- Bockhorn 1994 p 417. = Lindstead.

$$* \quad R = \underbrace{750 e^{-12100/T}}_{\frac{m^3}{m^2 \cdot s}} \cdot \underbrace{A}_{\frac{m^2}{m^3}} \cdot \underbrace{[C_2H_2]}_{kmol/m^3} \quad (=) \quad \frac{kmol}{m^3 \cdot s}$$

$$\longrightarrow \frac{R}{A} \cdot 2M_c \ (=) \left(\frac{kg\ soot}{m^2 \cdot s}\right) = 1500 e^{-12100/T} \underbrace{[C_2H_2]}_{\frac{kmol}{m^3}} / \underbrace{M_c}_{kg/kmol}$$

- $A = \underbrace{a_p}_{\frac{m^2}{part}} \underbrace{M_0}_{\#/m^3}$

Table 27.3

	f_v model	f_v exp
18% O_2	1E-7	3.7E-7
22% O_2	1.03E-6	1.1E-6
28% O_2	1.07E-5	2.2E-6