

Conservation of species in a mixture (solution, alloy)

Consider a mixture of species A, B, ... in a fixed volume V of masses m^α grams of species α , so total mass $m = \sum_\alpha m^\alpha$, density $\rho = \frac{m}{V}$ volumes V^α

$$\text{moles } n^\alpha = \frac{m^\alpha}{M^\alpha}$$

$$\text{total volume } V = \sum_\alpha V^\alpha$$

$$n = \sum_\alpha n^\alpha$$

$$\text{Partial densities (concentrations)}: \rho^\alpha = \frac{m^\alpha}{V} \Rightarrow \sum_\alpha \rho^\alpha = \frac{\sum m^\alpha}{V} = \frac{m}{V} = \rho$$

$$\text{Mass fractions: } C^\alpha = \frac{m^\alpha}{m} = \frac{\rho^\alpha}{\rho} \Rightarrow \sum_\alpha C^\alpha = \frac{\sum m^\alpha}{m} = \frac{m}{m} = 1$$

$$\text{mole fractions: } x^\alpha = \frac{n^\alpha}{n} \Rightarrow \sum_\alpha x^\alpha = 1$$

Mass flux of species α : $\vec{F}^\alpha = \rho^\alpha \vec{v}^\alpha$, \vec{v}^α = intrinsic molecular velocity of α (wild, Brownian motion)

$$(\text{quantity per unit volume}) \cdot (\text{its velocity}): \frac{g}{cm^3} \cdot \frac{cm}{sec} = \frac{g}{cm^2 \cdot sec}$$

(analogous to $\vec{D} = \epsilon \vec{E}$, $\vec{B} = \mu \vec{H}$, ...)

Conservation of species α : $\frac{\partial}{\partial t}(\rho^\alpha) + \nabla \cdot (\rho^\alpha \vec{v}^\alpha) = R^\alpha = \frac{\text{net rate of production of } \alpha \text{ per unit volume}}{\text{(by reactions, pumping, ...)}}$

$$\sum_\alpha \Rightarrow \frac{\partial}{\partial t}(n) + \nabla \cdot \left(\sum_\alpha \rho^\alpha \vec{v}^\alpha \right) = \sum_\alpha R^\alpha = 0 \text{ in closed system}$$

Total mass flux: $\sum_\alpha \rho^\alpha \vec{v}^\alpha =: \rho \vec{v}$ with mixture velocity $\vec{v} := \sum_\alpha \frac{\rho^\alpha}{\rho} \vec{v}^\alpha = \sum_\alpha C^\alpha \vec{v}^\alpha$
mass averaged barycentric velocity

To separate $\overset{\text{flow}}{\vec{F}^\alpha} = \rho^\alpha \vec{v}^\alpha = \overset{\text{non-flow}}{\rho^\alpha \vec{v}} + \overset{\text{non-flow}}{\rho^\alpha (\vec{v}^\alpha - \vec{v})}$ from (diffusion) (and give meaning to both): refer to mean flow

$$\overset{\text{flow}}{\vec{F}^\alpha} = \rho^\alpha \vec{v}^\alpha = \overset{\text{non-flow}}{\rho^\alpha \vec{v}} + \overset{\text{non-flow}}{\rho^\alpha (\vec{v}^\alpha - \vec{v})}$$

$$= \overset{\text{flow}}{\vec{F}_{\text{adv}}} + \overset{\text{non-flow}}{\vec{F}_{\text{non-advective}}}$$

$$= \overset{\text{flow}}{\rho^\alpha \vec{v}} + \overset{\text{non-flow}}{\vec{J}^\alpha} \quad \text{with } \overset{\text{non-flow}}{\vec{J}^\alpha} \text{ from a constitutive law}$$

$$\text{Note: } \sum_\alpha \overset{\text{non-flow}}{\vec{J}^\alpha} = \sum_\alpha \overset{\text{flow}}{\rho^\alpha \vec{v}^\alpha} - \sum_\alpha \overset{\text{flow}}{\rho^\alpha \vec{v}} = \overset{\text{flow}}{\rho \vec{v}} - \overset{\text{flow}}{\rho \vec{v}} = \overset{\text{non-flow}}{\vec{0}} \text{ always!}$$

e.g. for binary mixture $\overset{\text{flow}}{\vec{J}^A} + \overset{\text{flow}}{\vec{J}^B} = \overset{\text{flow}}{\vec{0}} \Rightarrow \overset{\text{non-flow}}{\vec{J}^B} = -\overset{\text{non-flow}}{\vec{J}^A}$ only one non-advective flu

Conservation of species α : $\frac{\partial \rho^\alpha}{\partial t} + \nabla \cdot (\rho^\alpha \vec{v} + \overset{\text{non-flow}}{\vec{J}^\alpha}) = R^\alpha$

Conservation of total mass: $\rho_t + \nabla \cdot (\rho \vec{v}) = 0$ in closed system
(continuity equation)

Conservation of momentum (equation of motion)

momentum = $m\vec{v}$ $\Rightarrow \rho\vec{v}$ = momentum per unit volume $\Rightarrow (\rho\vec{v})_t = \frac{\text{mass}}{\text{accel.}}$

Take $u = \vec{v}$ (one component at a time).

$$\text{Momentum flux: } \vec{F} = (\rho\vec{v})\vec{v} + \vec{T}$$

convective flux + stress tensor $\int_V T dx = \int_S T \cdot \vec{n} dA =$

$[\rho v_i v_j]$ symmetric $\begin{matrix} \\ 3 \times 3 \text{ matrix} \end{matrix}$ forces acting on boundary of a volume

$$\Rightarrow (\rho\vec{v})_t + \nabla \cdot [(\rho\vec{v})\vec{v} + \vec{T}] = \text{body forces} = \rho \vec{g} \text{ is Newton's 2nd law}$$

\vec{T} specified by constitutive law

Conservation of energy, $u = \epsilon = \text{internal + kinetic energy (per gram)}$
 $\rho\epsilon = \text{total energy per unit volume}$

$$\text{Energy flux: } \vec{F} = (\rho\epsilon)\vec{v} + \vec{Q}$$

convective non-convective (due to heat conduction, interdiffusion, radiation)

$$\Rightarrow (\rho\epsilon)_t + \nabla \cdot [(\rho\epsilon)\vec{v} + \vec{Q}] = \rho E = \text{energy source rate}$$

\vec{Q} from a constitutive law

Fourier law: $\vec{Q} = -k\vec{T}$ for conduction
 which brings in T

$\epsilon = \epsilon(T, P, \vec{C})$ from an equation of state (EoS)

$\vec{C} = (C^1, C^2, \dots, C^k) = \text{composition}$

$$\sum_{\alpha} C^{\alpha} = 1$$

Advection form of conservation:

Use continuity eqn. to break up the $\nabla \cdot [\rho u \vec{v}]$:

$$(\rho u)_t + \nabla \cdot [(\rho u) \vec{v}] = -\nabla \cdot \vec{\Phi} + \rho S$$

u = quantity per gram, $\rho u = \text{mass}$
 \vec{v} = (barycentric) velocity
 $\vec{\Phi}$ = non-adhesive fluxes

$$\underbrace{\rho_t u + \rho u_t}_{\text{LHS}} + u \nabla \cdot [\rho \vec{v}] + \rho \vec{v} \cdot \nabla u \quad \text{but } \rho_t + \nabla \cdot (\rho \vec{v}) = 0$$

$$\rho [u_t + \vec{v} \cdot \nabla u] = -\nabla \cdot \vec{\Phi} + \rho S$$

$$\Rightarrow \text{advection form: } u_t + \underbrace{\vec{v} \cdot \nabla u}_{\text{advection term}} = -\frac{1}{\rho} \nabla \cdot \vec{\Phi} + \frac{S}{\rho}$$

Note that LHS is the total time derivative of u in Lagrangian frame (moving along a flowline with \vec{v}):

$$\frac{Du}{Dt} := \frac{d}{dt} u(\vec{x}(t), t) = \nabla u \cdot \frac{d\vec{x}}{dt} + \frac{\partial u}{\partial t} = \vec{v} \cdot \nabla u + u_t$$

$$\text{So, in terms of the "material derivative"} \quad \frac{Du}{Dt} := \frac{d\vec{x}}{dt} + \vec{v} \cdot \nabla()$$

$$\frac{Du}{Dt} = -\frac{1}{\rho} \nabla \cdot \vec{\Phi} + S$$

So, the advection forms of the fundamental conservation laws are in Lagrangian frame:

$$\frac{DC^i}{Dt} = C_t^i + \vec{v} \cdot \nabla C^i = -\frac{1}{\rho} \nabla \cdot \vec{J}^i + \frac{1}{\rho} R^i$$

$$\frac{D\vec{v}}{Dt} = \vec{v}_t + (\vec{v} \cdot \nabla) \vec{v} = -\frac{1}{\rho} \nabla \cdot \vec{T} + \vec{g}$$

$$\frac{DE}{Dt} = E_t + \vec{v} \cdot \nabla E = -\frac{1}{\rho} \nabla \cdot \vec{Q} + E$$

$$\nabla \cdot \vec{v} = \sum_{j=1}^3 v_j \frac{\partial v_i}{\partial x_j}$$

Constitutive Laws

1. Fick's law: Diffusion: $\vec{j}^c = -D \nabla C^c$, $D = \text{diffusivity}$ [cm²/sec]

(+ $\rho \delta \nabla T + \rho \gamma \nabla P$ in general, usually negligible!)

thermal diffusion pressure diffusion
(Soret effect)

3. Fourier's law: Heat conduction: $\vec{Q} = -k \nabla T$, $k = \text{thermal conductivity}$ [$\frac{W}{m \cdot K}$]

(+ $\rho \beta \nabla C + \sum h^i j^i$)

Dufour effect partial enthalpy of v

5. Perfect inviscid fluid: $\vec{T}_{\infty} = P \vec{1}_{\infty}$ (no viscosity), $P = \text{pressure}$

4. D'Arcy Law:
in porous media flow

$$\vec{v}_x = -\lambda \left[\nabla P - g_x \vec{g} \right], \quad \lambda = \frac{k k_r}{\mu_x}, \quad k = \text{permeability of soil}$$

$\frac{k_r}{\mu_x}$ = relative permeability of fluid

μ_x = viscosity of phase x

ϕ = porosity

6. Newtonian fluid: $\vec{T}_{\infty} = P \vec{1}_{\infty} - \Pi$, $\Pi = \text{viscous stress tensor}$

$$= 2(\eta \vec{v}) \vec{1}_{\infty} + 2\mu \vec{D}$$

\vec{D} = deformation tensor

$$= \left[\frac{1}{2} (\nu_{ii} + \nu_{jj}) \right]_{ij}$$

7. Newtonian Gravitational potential (\vec{g}): $\vec{g} = -\nabla U$ Gauss law: $\nabla \cdot \vec{g} = -4\pi G\rho$, ρ = mass density

$$\Rightarrow \nabla^2 U = 4\pi G\rho$$
 Poisson eqn.

\vec{E} = electric field strength

V = electric potential (voltage)

$\vec{D} = \text{electric displacement field} = \epsilon \vec{E}$

ϵ = electrical permittivity of dielectric

σ = electrical conductivity

current density $\vec{J} = -\sigma \nabla V$

9. Magnetostatics: $\vec{B} = \mu \vec{H}$ \vec{H} = magnetic field strength

magnetic flux μ = magnetic permeability

Maxwell: $\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0}$, $\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$, $\nabla \cdot \vec{B} = 0$, $c^2 \nabla \times \vec{B} = \sigma \vec{E} + \frac{\partial \vec{E}}{\partial t}$

ρ = free charge density

ϵ_0 = dielectric const.

c = speed of light

σ = electrical conductivity