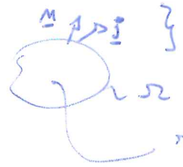
CHEMICAL POTENTIAL : Energy absorbed / released due to a change of the particle number

PRIMARY VARIABLE : $c \; \left[\frac{mol}{m^3}\right]$ $\Rightarrow$ CONJUGATE : $\mu \; \left[\frac{J}{mol}\right]$

•) MASS BALANCE



$\} \rightsquigarrow$ MOLECULES GOING OUT $\underline{j} \cdot \underline{n} \, dA$

$[\underline{j}] = \left[\frac{mol}{m^2 s}\right]$

$r \Rightarrow$ CHEMICAL REACTION PRODUCING C $\quad [r] = \left[\frac{mol}{s}\right]$

$c \Rightarrow c = c(\underline{x}, t)$

$$\int_\Omega \dot{c} \, dV = \int_\Omega r \, dV - \int_{\partial\Omega} \underline{j} \cdot \underline{n} \, dA = \int_\Omega r \, dV - \int_\Omega \mathrm{div}(\underline{j}) \, dV$$

$$\Rightarrow \int_\Omega \left(\dot{c} + \mathrm{div}(\underline{j}) - r \right) dV = 0 \quad \forall \Omega \Rightarrow \dot{c} = -\mathrm{div}(\underline{j}) + r$$

•) FIRST LAW OF THERMODYNAMICS $\Rightarrow$ ENERGY IS CONSERVED

$$\int_\Omega \dot{e} \, dV = \underbrace{\int_\Omega q_v \, dV}_{\substack{\text{HEAT-RATE VOL. SOURCE} \\ \text{(NEGATIVE IF REMOVED)}}} - \underbrace{\int_{\partial\Omega} \underline{q} \cdot \underline{n} \, dA}_{\substack{\text{HEAT-RATE LEAVING THE VOLUME} \\ \text{(NEGATIVE IF ENTERING)}}} + \underbrace{\int_\Omega \mu r \, dV}_{\substack{\text{ENERGY PROVIDED BY THE VOLUMETRIC} \\ \text{SOURCE OF PARTICLES} \\ \text{(NEGATIVE IF CONSUMED)}}} - \underbrace{\int_{\partial\Omega} \mu \underline{j} \cdot \underline{n} \, dA}_{\substack{\text{ENERGY LOSS DUE TO PARTICLES LEAVING} \\ \text{THE VOLUME} \\ \text{(NEGATIVE IF ENTERING)}}} + \underbrace{\int_\Omega \underline{f} \cdot \underline{\dot{u}} \, dV + \int_{\partial\Omega} \underline{t} \cdot \underline{\dot{u}}}_{\text{POWER OF EXTERNAL FORCES}}$$

RECALL $\int_{\partial\Omega} \underline{h} \cdot \underline{n} \, dA = \int_\Omega \mathrm{div}(\underline{h}) \, dV \Rightarrow + \int_{\partial\Omega} \underline{q} \cdot \underline{n} \, dA = \int_\Omega \mathrm{div}(\underline{q}) \, dV \; , \; \int_{\partial\Omega} \mu \underline{j} \cdot \underline{n} \, dA = \int_\Omega \mathrm{div}(\mu \underline{j})$

DEFINE : $q = q_v - \mathrm{div}(\underline{q}) \Rightarrow$ HEAT-RATE SUPPLIED TO THE SYSTEM

NOTE THAT : $\mathrm{div}(\mu \underline{j}) = \mu \, \mathrm{div}(\underline{j}) + \nabla\mu \cdot \underline{j} \Rightarrow \int_\Omega \mu r \, dV - \int_{\partial\Omega} \mu \underline{j} \cdot \underline{n} \, dA = \int_\Omega \mu \underbrace{(r - \mathrm{div}(\underline{j}))}_{= \dot{c} \text{ FROM MASS BALANCE}} - \nabla\mu \cdot \underline{j} \, d$

$$\int_\Omega \underline{f} \cdot \underline{\dot{u}} \, dV + \int_{\partial\Omega} \underline{t} \cdot \underline{\dot{u}} \, dA \underset{\uparrow}{=} \int_\Omega \underline{\underline{T}} : \underline{\underline{\dot{D}}} \, dV \overset{\text{VOIGT NOTATION}}{=} \int_\Omega \underline{\sigma} \cdot \underline{\dot{\varepsilon}} \, dV$$

PRINCIPLE OF VIRTUAL POWER $\quad \begin{cases} \underline{t} = \underline{\underline{T}} \underline{n} \\ \underline{\underline{D}} = \mathrm{Sym}(\nabla \underline{u}) \end{cases}$

AND $\begin{cases} \mathrm{div}(\underline{\underline{T}}) + \underline{f} = 0 \text{ in} \\ \underline{\underline{T}} \underline{n} = p \quad \text{on } \Sigma_p \\ \underline{u} = 0 \quad \text{on } \Sigma_u \end{cases}$

$$\Rightarrow \int_\Omega \dot{e} \, dV = \int_\Omega \left(q + \mu \dot{c} - \nabla\mu \cdot \underline{j} + \underline{\sigma} \cdot \underline{\dot{\varepsilon}} \right) V$$

$$\forall \Omega \Rightarrow \dot{e} = q + \mu \dot{c} - \nabla\mu \cdot \underline{j} + \underline{\sigma} \cdot \underline{\dot{\varepsilon}}$$

•) SECOND LAW OF THERMODYNAMICS

DERIVATION IN (5)

$$\dot{s} - \frac{q}{T} - \frac{\underline{q}}{T}\cdot\frac{\nabla T}{T} \geq 0 \Rightarrow T\dot{s} - q - \underline{q}\cdot\frac{\nabla T}{T} \geq 0$$

WITH $q = \dot{e} - \mu\dot{c} + \nabla\mu\cdot\underline{j} - \underline{\sigma}\cdot\dot{\underline{\varepsilon}} \Rightarrow \overbrace{T\dot{s} - \dot{e} + \mu\dot{c} - \nabla\mu\cdot\underline{j} + \underline{\sigma}\cdot\dot{\underline{\varepsilon}} - \underline{q}\cdot\frac{\nabla T}{T}}^{D} \geq 0$

➔ INTRODUCING $\psi(S_m, T) = e(s, S_m) - TS$ HELMHOLTZ FREE-ENERGY

S : VALUE OF ENTROPY AT EQUILIBRIUM

$\Rightarrow S = \underset{\hat{s}}{\operatorname{argmin}}\left(e(\hat{s}, S_m) - T\hat{s}\right)$

$$\Rightarrow \dot{e} = \dot{\psi} + \dot{T}S + T\dot{S} = \frac{\partial\psi}{\partial S_m}\dot{S}_m + \cancel{\underbrace{\frac{\partial\psi}{\partial T}}_{-S}\dot{T}} + \cancel{\dot{T}S} + T\dot{S} =$$

WITH $S_m = \{\varepsilon, c\}$ $= \dfrac{\partial\psi}{\partial\varepsilon}\dot{\varepsilon} + \dfrac{\partial\psi}{\partial c}\dot{c} + T\dot{S}$

$$\Rightarrow \text{T1)} \quad q + \mu\dot{c} - \nabla\mu\cdot\underline{j} + \underline{\sigma}\cdot\dot{\underline{\varepsilon}} - \frac{\partial\psi}{\partial\varepsilon}\dot{\varepsilon} - \frac{\partial\psi}{\partial c}\dot{c} - T\dot{s} = 0$$

$$\dot{s} = \frac{q}{T} + \frac{1}{T}\left(\left(\sigma - \frac{\partial\psi}{\partial\varepsilon}\right)\dot{\varepsilon} + \left(\mu - \frac{\partial\psi}{\partial c}\right)\dot{c}\right) - \frac{1}{T}\nabla\mu\cdot\underline{j} \qquad \boxed{\text{FIRST LAW}}$$

$$\Rightarrow \text{T2)} \quad D = \cancel{T\dot{s}} - \frac{\partial\psi}{\partial\varepsilon}\dot{\varepsilon} - \frac{\partial\psi}{\partial c}\dot{c} - \cancel{T\dot{s}} + \mu\dot{c} - \nabla\mu\cdot\underline{j} + \underline{\sigma}\cdot\dot{\underline{\varepsilon}} - \underline{q}\cdot\frac{\nabla T}{T} \geq 0$$

$$= \left(\sigma - \frac{\partial\psi}{\partial\varepsilon}\right)\dot{\varepsilon} + \left(\mu - \frac{\partial\psi}{\partial c}\right)\dot{c} - \nabla\mu\cdot\underline{j} - \underline{q}\cdot\frac{\nabla T}{T} \geq 0 \qquad \boxed{\text{SECOND LAW}}$$

•) CONSTITUTIVE LAWS FOR SATISFYING $D \geq 0$ FOR ANY ADMISSIBLE $\dot{\varepsilon}, \dot{c}, \underline{j}, \underline{q}$

$\dot{\varepsilon}$ AND $\dot{c}$ DO NOT HAVE A PREDEFINED SIGN $\Rightarrow$ THE ONLY POSSIBILITY TO HAVE:

$$\left.\begin{array}{l}\left(\sigma - \frac{\partial\psi}{\partial\varepsilon}\right)\dot{\varepsilon} \geq 0 \\ \left(\mu - \frac{\partial\psi}{\partial c}\right)\dot{c} \geq 0\end{array}\right\} \text{IS TO REQUIRE:} \quad \boxed{\sigma = \frac{\partial\psi}{\partial\varepsilon} \qquad \mu = \frac{\partial\psi}{\partial c}}$$

$$\left.\begin{array}{l}\underline{j} \text{ AND } \nabla\mu \\ \underline{q} \text{ AND } \nabla T\end{array}\right\} \text{OPPOSITE VECTORS}$$

$$\Downarrow$$

$$\left[\begin{array}{ll}\underline{q} = -K_T\nabla T & \text{(FOURIER'S LAW)} \\ \underline{j} = -K_c\nabla\mu & \end{array}\right.$$

SPECIFIC MODELS (NO HEAT)

UNIVERSAL GAS CONSTANT $R = 8.314 \, \frac{J}{mol\,K}$

$$\underbrace{S'_m = \{\varepsilon, c\}} \Rightarrow \psi(\varepsilon, c) = \psi_{el}(\varepsilon) + \psi_{ch}(c) = \frac{1}{2}\varepsilon^T \mathbb{C} \varepsilon + (\underset{\sim}{\mu_0} - RT)c + RT\frac{c}{\underset{\sim}{c_{eq}}}\ln\left(\frac{c}{c_{eq}}\right)$$

- NO INTERACTION
- ONE CHEM. SPECIES

μ_0: REF. POTENTIAL (DEPENDING ON T AND STATE OF THE SYSTEM)

c_{eq}: EQUILIBRIUM CONCENTRATION

$\Rightarrow$ CONSTITUTIVE LAWS:

$$\sigma = \frac{\partial \psi_{el}}{\partial \varepsilon} = \mathbb{C}\varepsilon$$

$$\mu = \frac{\partial \psi_{ch}}{\partial c} = \mu_0 + RT\ln\left(\frac{c}{c_{eq}}\right)$$

} THIS IS DERIVED FROM THE DIFFUSION FORCE, THAT IS f_d ACTING ON A "GRAM-ION" OF PARTICLES (= AVOGADRO'S NUMBER) DUE TO DIFFUSION (NO ELECTROSTATICS):

$\frac{N}{mol} = \frac{J}{mol \cdot m} \Leftarrow \frac{J}{mol}\frac{m^3}{mol}\frac{mol}{m^4}$

$$\Rightarrow f_d = -RT\frac{1}{c}\nabla c = -RT\,\nabla\left(\ln\left(\frac{c}{c_{eq}}\right)\right)$$

μ È LA FUNZIONE POTENZIALE DEL CAMPO VETTORIALE f_d $\left\{ \nabla\mu = -f_d \right.$

VALID (TOGETHER WITH μ) FOR PERFECT GASES OR DILUITE SOLUTIONS $\Leftarrow$ { NEGLECTS INTERACTION BETWEEN MOVING PARTICLES AND IT CAN BE DERIVED FROM THE DIFFUSION OF IONS THROUGH A MEMBRANE (BY TEORELL) OR BROWNIAN MOTIONS (BY EINSTEIN)

$$\underset{\frac{mol}{m^2 s}}{j} = -\underset{\frac{mol^2}{J s m}}{K_c}\,\underset{\frac{J}{mol \cdot m}}{\nabla\mu} = c_q a\, v_d = c_q a\,\overbrace{(m f_d)}^{K_c\,(-\nabla\mu)}$$

$K_c \to$ FLUX PROPORTIONAL TO

PROPORZIONALE A:
- CONCENTRAZIONE
- ATTIVITÀ MOLECOLE
- VELOCITÀ

$m = \frac{v}{f} \Rightarrow [m] = \frac{m}{s}\cdot\frac{mol}{N} = \frac{m^2 \cdot mol}{J s}$

{ MOBILITY PARAMETER $m \Rightarrow$ FOR $f_d \rightsquigarrow$ VELOCITY IS $m f_d$

ACTIVITY COEFFICIENT $a = e^{\frac{\mu-\mu_0}{RT}}$ (EYRING, 194

$$\Rightarrow K_c = \underset{\frac{mol \cdot m^2}{J s}}{m} \cdot \underset{[-]}{a} \cdot \underset{\frac{mol}{m^3}}{c_{eq}}$$

FOR DILUITE SOLUTIONS $\left(\mu = \mu_0 + RT\ln\left(\frac{c}{c_{eq}}\right)\right)$: $a = \frac{c}{c_{eq}}$, $\nabla\mu = \frac{RT}{c}\nabla c$

$$\Rightarrow j = -\underbrace{m\,\frac{\cancel{c}}{\cancel{c_{eq}}}\,\cancel{c_{eq}}\,\frac{RT}{\cancel{c}}}\,\nabla c = -D\,\nabla c \qquad \text{FICK'S LAW}$$

$D = mRT \Rightarrow$ DIFFUSION PARAMETER $[D] = \left[\frac{m^2}{s}\right]$

$\Rightarrow$ SOLVING EQUATIONS:

- EQUILIBRIUM: $\mathrm{div}(\mathbb{C} : \underline{\underline{D}}) + \underline{f} = 0$ WITH $\overbrace{(\mathbb{C} : \underline{\underline{D}})}^{\underline{\underline{T}}}\,\underline{n} = \underline{p}$ ON Σ_p

  $\underline{\underline{D}} = \mathrm{Sym}(\nabla u)$ WITH $\underline{u} = \underline{0}$ ON Σ_u

- MASS BALANCE: $\dot{c} = -\mathrm{div}(D\nabla c) + r$ IN Ω WITH $\left\{ \begin{array}{ll} c = \hat{c} \text{ ON } \Sigma_c & \text{DIRICHLET (ESSENTIAL)} \\ D\nabla c = \hat{j} \text{ ON } \Sigma_j & \text{NEUMANN (NATURAL)} \end{array} \right.$

  OR

  $D\nabla c = K_j(c - c_{ext})$ ROBIN (MIXED)

Σ_j { PRESCRIBE FLUX

PRESCRIBED CONC. { Σ_c

IF $D = \text{CONST} \Rightarrow \dot{c} = -D\underset{\text{LAPLACIAN}}{\underline{\Delta c}} + r$

$$\underbrace{S'_m}_{} = \{ \underline{\varepsilon}, C_1, C_2 \}$$

- NO INTERACTION BETWEEN MECHANICS AND TRANSPORT
- MIXTURE (TWO SPECIES) $\rightsquigarrow C_{mix} = C_1 + C_2$

$$\psi(\underline{\varepsilon}, C_1, C_2) = \psi_{ee}(\underline{\varepsilon}) + \psi_{C_1}(\underbrace{C_1, C_2}) + \psi_{C_2}(\underbrace{C_1, C_2})$$

$\hookrightarrow$ INTERACTION BTW. THE TWO SPECIES

$$\psi_{C_1}(C_1, C_2) = \mu_{01} C_1 + RT\, C_1 \ln\left(\frac{C_1}{C_1+C_2}\right), \quad \psi_{C_2}(C_1, C_2) = \mu_{02} C_2 + RT\, C_2 \ln\left(\frac{C_2}{C_1+C_2}\right)$$

$\Rightarrow$ CONSTITUTIVE LAWS: (CHEMICAL)

$$\mu_1 = \frac{\partial \psi}{\partial C_1} = \mu_{01} + RT \ln\left(\frac{C_1}{C_1+C_2}\right) + \overbrace{\cancel{\frac{RT\,C_1}{C_1}}}^{RT\,C_1\,\partial\ln(C_1)} \overbrace{- \cancel{\frac{RT\,C_1}{C_1+C_2}}}^{-RT\,C_1\,\partial\ln(C_1+C_2)} \overbrace{- \cancel{\frac{RT\,C_2}{C_1+C_2}}}^{-RT\,C_2\,\partial\ln(C_1+} =$$

$$= \mu_{01} + RT \ln\left(\frac{C_1}{C_1+C_2}\right)$$

$$\mu_2 = \frac{\partial \psi}{\partial C_2} = \mu_{02} + RT \ln\left(\frac{C_2}{C_1+C_2}\right)$$

$$\underline{j}_1 = -K_{C_1} \nabla \mu_1 \quad \text{WITH} \quad K_{C_1} = m_1 \cdot a_1 (C_1 + C_2) = m_1\, e^{\overbrace{\frac{\mu_1 - \mu_{01}}{RT}}^{\frac{C_1}{C_1+C_2}}} (C_1+C_2) = m_1$$

$$\Rightarrow \underline{j}_1 = -m_1 C_1 RT \nabla\left(\ln\left(\frac{C_1}{C_1+C_2}\right)\right) \overset{D_1 = m_1 RT}{=} -D_1 \cancel{C_1} \cdot \frac{C_1+C_2}{\cancel{C_1}} \left(\frac{\nabla C_1}{C_1+C_2} - \frac{C_1}{(C_1+C_2)^2} \nabla C_{mix}\right)$$

$$= -D_1 \left(\nabla C_1 - \frac{C_1}{C_1+C_2} \nabla (C_1 + C_2)\right)$$

$$\underline{j}_2 = -D_2 \left(\nabla C_2 - \frac{C_2}{C_1+C_2} \nabla (C_1 + C_2)\right)$$

IF IT HOLDS: $C_1 \ll C_2 \Rightarrow \frac{C_1}{C_1+C_2} \approx 0 \Rightarrow \underline{j}_1 \approx -D_1 \nabla C_1$

$\underbrace{S_m}_{} = \{ \underline{\varepsilon}_e, \underline{\varepsilon}_i, c \}$ WITH $\underset{\sim}{\underline{\varepsilon}} = \underline{\varepsilon}_e + \underline{\varepsilon}_i$ AND $\underbrace{\underline{\underline{D}}_i = \frac{\Delta}{3}(c - c_{eq})\underline{\underline{I}}}_{} \Rightarrow \underline{\varepsilon}_i$

$\underline{\underline{D}} = Sym(\nabla u)$

CHANGE OF VOLUME ASSOCIATED WITH 1 mol/m³ VARIATION OF C over C_{eq}

- INTERACTION BTW. MECHANICS AND TRANSPORT

IF $c \neq c_{eq} \Rightarrow \underline{\varepsilon}_i \neq 0$

CHANGE OF VOLUME $Tr(\underline{\underline{D}}_i)$ $\left\{ \begin{array}{l} c > c_{eq} \Rightarrow \text{DILATATION (ISOTROPIC)} \\ c < c_{eq} \Rightarrow \text{SHRINKING} \end{array} \right\} \Delta(c - c_{eq})$

$$\Rightarrow \psi(\underline{\varepsilon}_e, \underline{\varepsilon}_i, c) = \psi_{ee}(\underline{\varepsilon}_e) + \psi_{ch}(c)$$

$$\text{with } \psi_{ee}(\underline{\varepsilon}_e) = \frac{1}{2} \underline{\varepsilon}_e^T \mathbb{C} \underline{\varepsilon}_e \quad \text{AND} \quad \psi_{ch}(c) = (\mu_0 - RT)c + RT \frac{c}{c_{eq}} \ln\left(\frac{c}{c_{eq}}\right)$$

$\varepsilon_i^{vol} \Downarrow \dot{\varepsilon}_i^{vol} = \Delta \dot{c}$

•) II LAW OF THERMODYNAMICS

ATTENTION : $\dot{\psi} = \frac{\partial \psi_{ee}}{\partial \underline{\varepsilon}_e} \cdot \dot{\underline{\varepsilon}}_e + \frac{\partial \psi_{ch}}{\partial c} \dot{c}$

$$\underbrace{\underline{\sigma} \cdot \dot{\underline{\varepsilon}}}_{} = \underline{\underline{T}} : \dot{\underline{\underline{D}}} = \underline{\underline{T}} : (\dot{\underline{\underline{D}}}_e + \dot{\underline{\underline{D}}}_i) = \underline{\underline{T}} : \dot{\underline{\underline{D}}}_e + \underbrace{\underline{\underline{T}} : \dot{\underline{\underline{D}}}_i}_{} = \underline{\sigma} \cdot \dot{\underline{\varepsilon}}_e - p \dot{\varepsilon}_i^{vol}$$

POWER OF INTERNAL FORCES
(σ PRODUCES POWER FOR THE TOTAL $\dot{\varepsilon}$)

$$\frac{\Delta}{3} \dot{c} \, \underbrace{\underline{\underline{T}} : \underline{\underline{I}}}_{Tr(\underline{\underline{T}})} = -p \Delta \dot{c} = -p \dot{\varepsilon}_i^{vol}$$

$p := -\frac{Tr(\underline{\underline{T}})}{3}$ HYDROSTATIC PRESSURE (POSITIVE IF)

$$\Rightarrow D = -\frac{\partial \psi_{ee}}{\partial \underline{\varepsilon}_e} \dot{\underline{\varepsilon}}_e - \frac{\partial \psi_{ch}}{\partial c} \dot{c} + \mu \dot{c} + \overbrace{\underline{\sigma} \cdot \dot{\underline{\varepsilon}}_e - p \underset{\sim}{\dot{\varepsilon}_i^{vol}}}^{\underline{\sigma} \cdot \dot{\underline{\varepsilon}}} - \nabla \mu \cdot \underline{j} - \underline{q} \cdot \frac{\nabla T}{T} \geq 0$$

$\hookrightarrow = \Delta \dot{c}$

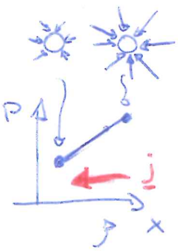
$$= \left(\underline{\sigma} - \frac{\partial \psi_{ee}}{\partial \underline{\varepsilon}_e}\right) \dot{\underline{\varepsilon}}_e + \left(\mu - \Delta p - \frac{\partial \psi_{ch}}{\partial c}\right) \dot{c} - \nabla \mu \cdot \underline{j} - \underline{q} \cdot \frac{\nabla T}{T} \geq 0$$

$\Rightarrow$ CONSTITUTIVE LAWS : $\underline{\sigma} = \frac{\partial \psi_{ee}}{\partial \underline{\varepsilon}_e}$ $\quad \mu^{act} = \mu - \Delta p = \frac{\partial \psi_{ch}}{\partial c} \Rightarrow \mu = \frac{\partial \psi_{ch}}{\partial c} + \Delta p$

AND THEN $\underline{\sigma} = \mathbb{C} \underline{\varepsilon}_e$ AND $\mu = \mu_0 + RT \ln\left(\frac{c}{c_{eq}}\right) + \Delta p$

$$\Rightarrow \underline{j} = -mc\left(RT \frac{\nabla c}{c} + \Delta \nabla p\right) = -D \nabla c - \underbrace{\frac{Dc}{RT} \Delta \nabla p}_{}$$

$\hookrightarrow$ MOVEMENT DUE TO ∇p



$\Rightarrow$ SOLVING EQUATIONS :

- EQUILIBRIUM : $div(\mathbb{C} : \underline{\underline{D}}_e) + \underline{f} = 0$ with $(\mathbb{C} : \underline{\underline{D}}_e)\underline{n} = \hat{\underline{t}}$ ON Σ_t

$\underline{\underline{D}} = Sym(\nabla u) = \underline{\underline{D}}_e + \underline{\underline{D}}_i$ WITH $\underline{\underline{D}}_i = \frac{\Delta}{3}(c - c_{eq})\underline{\underline{I}}$ AND $\underline{u} = 0$ on Σ_u

- MASS BALANCE : $\dot{c} = -div\left(D \nabla c + \frac{c\Delta}{RT} \nabla p\right) + r$ WITH $c = \hat{c}$ on Σ_c

$\underline{j} = \hat{\underline{j}}$ ON Σ_j