2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 22

Room 3-442
Friday, April 26, 11:00am - 1:00pm

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Nonequilibrium in heat, mass, and charge transfer

Logic and ingredients of the construction

Parallel logic in the construction of nonequilibrium theories:

Heat transfer vs chemical kinetics

Heat transfer in a pure solid

Energy balance: $\dfrac{\partial \rho u^*}{\partial t} = -\underline{\nabla}\cdot\underline{J}_E$

Entropy balance: $\dfrac{\partial \rho s^*}{\partial t} = -\underline{\nabla}\cdot\underline{J}_S + \sigma$

No change in composition: $\dfrac{\partial c}{\partial t} = 0$

Gibbs relation: $\mathrm{d}(\rho u^*) = T\,\mathrm{d}(\rho s^*) + \mu\,\mathrm{d}c$

$$\frac{\partial \rho u^*}{\partial t} = T\,\frac{\partial \rho s^*}{\partial t} + \mu\,\frac{\partial c}{\partial t}$$

Combine: $T\,\sigma = T\,\underline{\nabla}\cdot\underline{J}_S - \underline{\nabla}\cdot\underline{J}_E$

Assume heat: $\underline{J}_E = \underline{q}''\quad \underline{J}_S = \underline{q}''/T$

$$\underline{\nabla}\cdot\underline{J}_E = \underline{\nabla}\cdot\underline{q}''$$

$$\underline{\nabla}\cdot\underline{J}_S = \underline{\nabla}\cdot(\underline{q}''/T) = (\underline{\nabla}\cdot\underline{q}'')/T + \underline{q}''\cdot\underline{\nabla}(1/T)$$

Substitute and obtain: $\sigma = \underline{q}''\cdot\underline{\nabla}(1/T)$

Assume Fourier law: $\underline{q}'' = \underline{\underline{L}}\cdot\underline{\nabla}(1/T)$

Onsager reciprocity: $\underline{\underline{L}}^{\mathrm{T}} = \underline{\underline{L}}$

$\underline{q}'' = -\underline{\underline{k}}\cdot\underline{\nabla}T$ with

$$\underline{\underline{k}} = \underline{\underline{L}}/T^2 \quad \underline{\underline{R}} = \underline{\underline{k}}^{-1}/T^2 \quad \underline{\underline{R}} = \underline{\underline{L}}^{-1}$$

$$\sigma = \underline{\nabla}(1/T)\cdot\underline{\underline{L}}\cdot\underline{\nabla}(1/T) = \underline{q}''\cdot\underline{\underline{R}}\cdot\underline{q}''$$

Chemical kinetics in isolated mixture

Energy balance: $\dfrac{\partial U}{\partial t} = 0$

Entropy balance: $\dfrac{\partial S}{\partial t} = \dot{S}_{\mathrm{irr}}$

Proportionality relations: $\dot{n}_i = \sum_j \nu_i^{(j)}\dot{\epsilon}_j$

Assume SES$_{\mathbf{off}}$: $S = S_{\mathrm{off}}(U, V, \boldsymbol{n})$

$$\frac{\partial S_{\mathrm{off}}}{\partial t} = \sum_i \frac{\partial S_{\mathrm{off}}}{\partial n_i}\dot{n}_i = -\frac{1}{T}\sum_i \mu_i \dot{n}_i$$

$$= -\frac{1}{T}\sum_i \mu_i \sum_j \nu_i^{(j)}\dot{\epsilon}_j = \sum_j Y_j\,\dot{\epsilon}_j$$

Combine: $\dot{S}_{\mathrm{irr}} = \sum_j Y_j\,\dot{\epsilon}_j$

Assume Arrhenius law: $\dot{\epsilon}_j = \dot{\epsilon}_j^+ - \dot{\epsilon}_j^-$

$$\frac{Y_j}{R} = \ln\frac{\dot{\epsilon}_j^+}{\dot{\epsilon}_j^-}$$

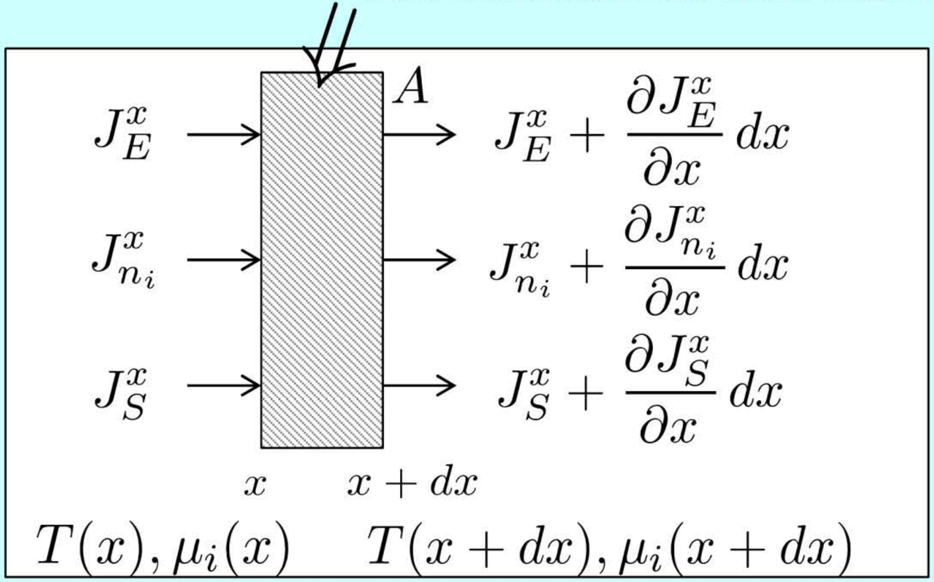
$$\dot{S}_{\mathrm{irr}} = R\sum_j(\dot{\epsilon}_j^+ - \dot{\epsilon}_j^-)\ln\frac{\dot{\epsilon}_j^+}{\dot{\epsilon}_j^-}$$

Nonequilibrium in heat, mass, and charge transfer

General balance equations for the extensive properties of a continuum

Balance equations for 1D heat and mass transfer

this infinitesimal fluid element has volume $\delta V = A\,dx$



has energy, amounts, and entropy

$$\delta E = \rho u^* \delta V = \rho u^* A\,dx$$

$$\delta n_i = c_j\,\delta V = c_j\,A\,dx$$

$$\delta S = \rho s^* \delta V = \rho s^* A\,dx$$

and source terms

$$\delta\dot{\varepsilon} = r_k\,\delta V = r_k\,A\,dx$$

$$\delta\dot{S}_{\rm irr} = \dot{s}_{\rm irr}'''\,\delta V = \dot{s}_{\rm irr}'''\,A\,dx$$

$$\frac{d(\delta E)}{dt} = -A\frac{dJ_E^x}{dx}\,dx \qquad \frac{d(\delta n_i)}{dt} = -A\frac{dJ_{n_i}^x}{dx}\,dx + \sum_k \nu_{ik}\delta\dot{\varepsilon}_k \qquad \frac{d(\delta S)}{dt} = -A\frac{dJ_S^x}{dx}\,dx + \delta\dot{S}_{\rm irr}$$

$$\frac{\partial \rho u^*}{\partial t} = -\frac{dJ_E^x}{dx} \qquad \frac{\partial c_i}{\partial t} = -\frac{dJ_{n_i}^x}{dx} + \sum_k \nu_{ik} r_k \qquad \frac{\partial \rho s^*}{\partial t} = -\frac{dJ_S^x}{dx} + \dot{s}_{\rm irr}'''$$

Ingredients of the general balance equations for the extensive properties of a continuum:

Rate of change of a generic extensive property of a continuum

Consider the material contained at time t in volume $\Sigma_m(t)$, delimited by the surface $\partial\Sigma_m(t)$ (with local outward normal unit vectors denoted by $\underline{n}$). Assume that in the **material volume** we can define the mass density (mass per unit volume) field $\rho\left(\underline{x},t\right)$. We say that property A is “extensive” if its instantaneous value for the material inside Σ_m can be written as

$$A(t) = \int_{\Sigma_m(t)} \rho\left(\underline{x},t\right)\, a^*(\underline{x},t)\,\mathrm{d}V$$

where $a^*\left(\underline{x},t\right)$ is the locally averaged specific property A per unit mass.

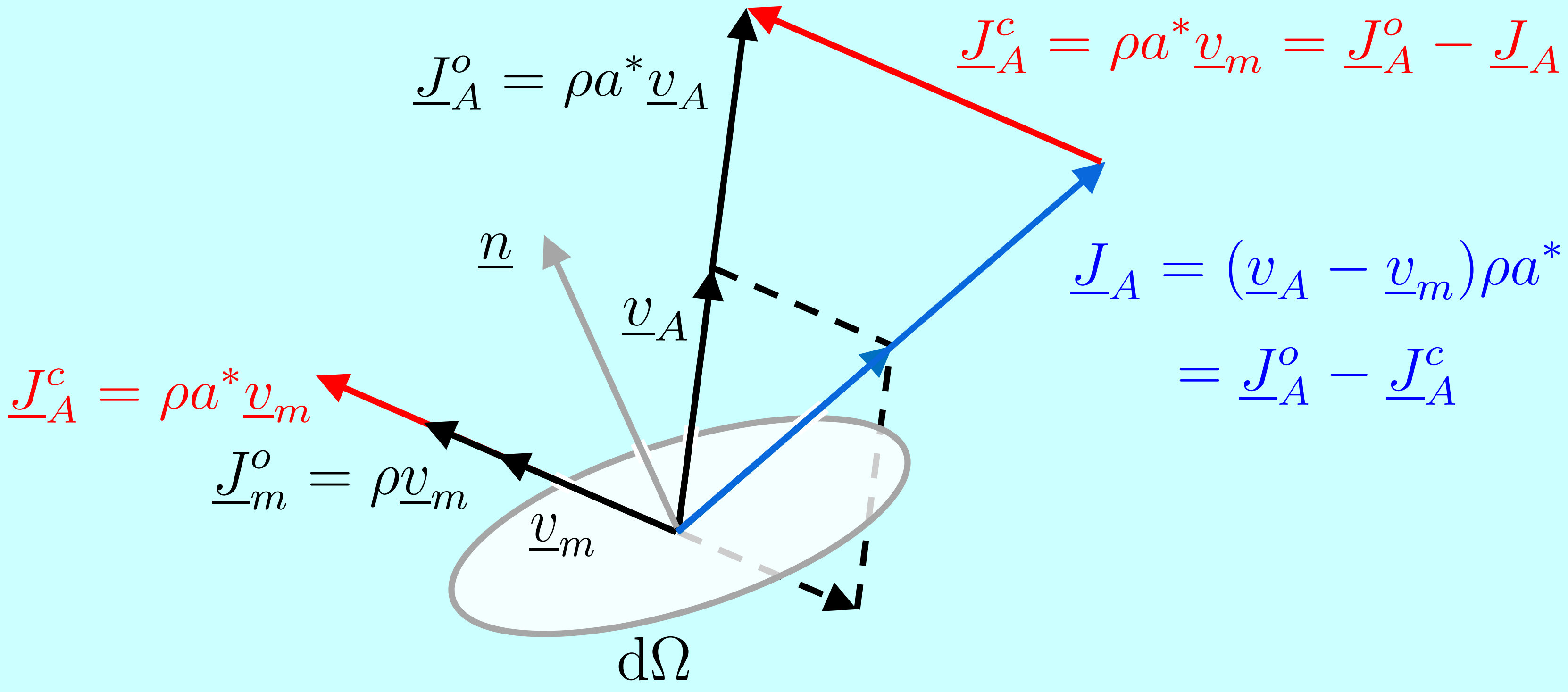
The rate of change of the above integral value of property A for the material volume $\Sigma_m(t)$ can be written as follows (**Reynolds theorem**)

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Sigma_m(t)} \rho a^*\,\mathrm{d}V = \int_{\Sigma_m(t)} \frac{\partial \rho a^*}{\partial t}\,\mathrm{d}V + \oint_{\partial\Sigma_m(t)} (\underline{v}_{\partial\Sigma_m}\cdot\underline{n})\rho a^*\,\mathrm{d}\Omega = \int_{\Sigma_m(t)} \left[\frac{\partial \rho a^*}{\partial t} + \underline{\nabla}\cdot(\rho a^* \underline{v}_m)\right]\mathrm{d}V$$

where in the last step we used the divergence theorem and the fact that for a material volume the velocity $\underline{v}_{\partial\Sigma_m}$ of the area element along its boundary surface coincides with the barycentric flow velocity $\underline{v}_m$ of the continuum.

Ingredients of the general balance equations for the extensive properties of a continuum:

Diffusive and convective fluxes in terms of transport velocities



Amount $\delta A^{\underline{n}\rightarrow}$ of property A that crosses an infinitesimal planar surface of area $\mathrm{d}\Omega$ in the direction of the unit normal $\underline{n}$ during the time interval between t and $t+\mathrm{d}t$

$$\delta A^{\underline{n}\rightarrow} = (\underline{v}_A \cdot \underline{n})\rho a^* \, \mathrm{d}\Omega \, \mathrm{d}t = (\underline{J}_A^o \cdot \underline{n}) \, \mathrm{d}\Omega \, \mathrm{d}t$$

This slide was added after Lecture 22. It is repeated and illustrated in Lecture 23.

Ingredients of the general balance equations for the extensive properties of a continuum:

Diffusive and convective fluxes in terms of transport velocities

With each extensive property A we associate:

- The "property–A **transport velocity**" field with respect to an inertial laboratory reference frame, denoted by $\underline{v}_A(\underline{x},t)$, such that the amount $\delta A^{\underline{n}\rightarrow}$ of property A that crosses an infinitesimal planar surface of area $\mathrm{d}\Omega$ in the direction of its outward unit normal $\underline{n}$ during the time interval between t and $t+\mathrm{d}t$ is given by

$$\delta A^{\underline{n}\rightarrow} = (\underline{v}_A \cdot \underline{n})\rho a^*\,\mathrm{d}\Omega\,\mathrm{d}t = (\underline{J}^o_A \cdot \underline{n})\,\mathrm{d}\Omega\,\mathrm{d}t \qquad \text{where} \qquad \underline{J}^o_A = \rho a^* \underline{v}_A$$

defines the Lagrangian flux of property A. In particular, for $A = m$, the mass transport velocity $\underline{v}_m(\underline{x},t)$ is the barycentric velocity field, in fluid mechanics usually simply called the (Eulerian) velocity field.

- The "property–A **diffusive flux**" field (relative to the local barycentric velocity)

$$\underline{J}_A = (\underline{v}_A - \underline{v}_m)\rho a^* = \underline{J}^o_A - \rho a \underline{v}_m$$

For $a^* = \underline{v}_m$, the momentum diffusive flux $\underline{J}_{\underline{v}_m}$ is the pressure tensor $\underline{\underline{P}}$, the negative of the stress tensor $\underline{\underline{\tau}}$ of fluid mechanics, usually split into the isotropic mechanical pressure and the deviatoric stress tensor $\underline{J}_{\underline{v}_m} = \underline{\underline{P}} = -\underline{\underline{\tau}} = p_m\underline{\underline{\delta}} - \underline{\underline{\tau}}'$, where $p_m = \mathrm{Trace}(\underline{\underline{P}})/3$ is called the mechanical pressure. Note also that $\underline{J}_m = 0$ and therefore

$$\sum_i M_i \underline{J}_{n_i} = 0 \qquad \text{or, equivalently,} \qquad \sum_i \underline{J}_{m_i} = 0$$

- The "property–A **convective flux**" field (due to the local barycentric velocity)

$$\underline{J}^c_A = \rho a^* \underline{v}_m = \underline{J}^o_A - \underline{J}_A$$

For $A = \underline{v}_m$, the convective momentum flux is the dyadic tensor $\underline{J}^c_{\underline{v}_m} = \rho \underline{v}_m \underline{v}_m$.

Ingredients of the general balance equations for the extensive properties of a continuum:

Local source/sink densities account for the effects of collisions, and short and long range forces

With each extensive property A we also associate:

- The "property–A **source/sink density**" field $\sigma_A(\underline{x},t)$ representing the local rate of production (if positive) or consumption (if negative) per unit volume. It may also be denoted by $\dot{a}'''$ and/or split into the sum of two source terms

$$\dot{a}''' = \sigma_A(\underline{x},t) = \sigma_A^i(\underline{x},t) + \sigma_A^e(\underline{x},t)$$

where σ_A^i is typically linked to local effects of short range forces and the general local collisional redistribution mechanisms that drive the local state towards stable equilibrium, whereas σ_A^e is typically linked to local effects of long range external forces such as gravitational and electromagnetic. Clearly, if A is a conserved property the source terms must vanish everywhere, $\sigma_A^i(\underline{x},t) = 0$.

- The "**balance equation** for extensive property A" expressing the notion that a change in time of $A(t)$ for the material volume can only be due to either net overall effects of source/sink / production/consumption of A within the volume or overall effects of net convection or diffusive fluxes of A across its boundary surface

$$\frac{\mathrm{d}A(t)}{\mathrm{d}t} = \int_{\Sigma_m(t)} \sigma_A\,\mathrm{d}V - \oint_{\partial\Sigma_m(t)} [(\underline{v}_A - \underline{v}_{\partial\Sigma_m})\cdot\underline{n}]\rho a^*\,\mathrm{d}\Omega = \int_{\Sigma_m(t)} [\sigma_A - \underline{\nabla}\cdot\underline{J}_A]\,\mathrm{d}V$$

where in the last step we used the divergence theorem, the definition of the diffusive flux $\underline{J}_A$, and the fact that for a material volume $\underline{v}_{\partial\Sigma_m} = \underline{v}_m$.

- Using the Reynolds theorem for the lhs yields the integral balance equation for A

$$\int_{\Sigma_m(t)} \left[\frac{\partial\rho a^*}{\partial t} + \underline{\nabla}\cdot(\rho a^*\underline{v}_m)\right]\mathrm{d}V = \int_{\Sigma_m(t)} [\sigma_A - \underline{\nabla}\cdot\underline{J}_A]\,\mathrm{d}V$$

General balance equations for an extensive property of a continuum

Given an extensive property A with instantaneous value for the material inside Σ_m given by

$$A(t) = \int_{\Sigma_m(t)} \rho\,(\underline{x},t)\; a^*(\underline{x},t)\,\mathrm{d}V$$

the integral balance equation for A

$$\int_{\Sigma_m(t)} \left[\frac{\partial \rho a^*}{\partial t} + \underline{\nabla}\cdot(\rho a^* \underline{v}_m)\right] \mathrm{d}V = \int_{\Sigma_m(t)} [\sigma_A - \underline{\nabla}\cdot\underline{J}_A]\,\mathrm{d}V$$

must hold for an arbitrary material volume $\Sigma_m(t)$ and hence it implies the indefinite A balance equation

$$\frac{\partial \rho a}{\partial t} + \underline{\nabla}\cdot(\rho a^* \underline{v}_m) = \sigma_A - \underline{\nabla}\cdot\underline{J}_A$$

Using the relation

$$\underline{J}_A = \underline{J}_A^o - \rho a^* \underline{v}_m$$

between the Lagrangian flux $\underline{J}_A^o$, the diffusive flux $\underline{J}_A$, and the convective flux $\underline{J}_A^c = \rho a^* \underline{v}_m$, we may rewrite it as either

$$\frac{\partial \rho a^*}{\partial t} + \underline{\nabla}\cdot\underline{J}_A^o = \sigma_A \qquad \text{or} \qquad \rho\frac{Da^*}{Dt} + \underline{\nabla}\cdot\underline{J}_A = \sigma_A$$

where we defined the **material derivative**

$$\frac{Da^*}{Dt} = \frac{\partial a^*}{\partial t} + \underline{v}_m\cdot\underline{\nabla} a^*$$

which represents the rate of change of the specific density of A as perceived by the fluid element while it evolves along its trajectory (pathline).

Interrelations between alternative variables used to account for composition, and on the definition of barycentric velocity

		in terms of mole fractions	in terms of mass fractions	in terms of molar densities	in terms of mass densities
Mole fraction of i	y_i	$\equiv n_i/n$	$M x_i/M_i$	c_i/c	$\rho_i M/\rho\, M_i$
Mass fraction of i	x_i	$M_i y_i/M$	$\equiv m_i/m$	$M_i c_i/M c$	ρ_i/ρ
Molar density of i	c_i	$y_i\, c$	$\rho\, x_i/M_i$	$\equiv n_i/V$	ρ_i/M_i
Mass density of i	ρ_i	$M_i y_i\, c$	$\rho\, x_i$	$M_i c_i$	$\equiv m_i/V$
Charge density of i	ρ_{q_i}	$F z_i y_i\, c$	$\rho F z_i x_i/M_i$	$\equiv q_i/V = F z_i c_i$	$F z_i \rho_i/M_i$
Mean molar mass	M	$\equiv \sum_i M_i y_i$	$1/\sum_i (x_i/M_i)$	$\sum_i M_i c_i/c$	$\rho/\sum_i (\rho_i/M_i)$
Total mole density	c	$\equiv n/V$	ρ/M	$\sum_i c_i$	$\sum_i \rho_i/M_i$
Total mass density	ρ	$M c$	$\equiv m/V$	$\sum_i M_i c_i$	$\sum_i \rho_i$
Total charge density	ρ_q	$cF \sum_i z_i y_i$	$\rho F \sum_i z_i x_i/M_i$	$\equiv q/V = F \sum_i z_i c_i$	$F \sum_i z_i \rho_i/M_i$
Barycentric velocity	$\underline{v}_m$	$\sum_i M_i y_i \underline{v}_i/M$	$\equiv \sum_i x_i \underline{v}_i$	$\sum_i M_i c_i \underline{v}_i/M c$	$\sum_i \rho_i \underline{v}_i/\rho$

The **barycentric velocity** is defined by

$$\underline{v}_m = \sum_i x_i \underline{v}_i$$

where $\underline{v}_i = \underline{v}_{m_i} = \underline{v}_{n_i}$ is the velocity of (mole and mass) transport of species i, such that $\underline{J}^o_{n_i} = c_i \underline{v}_i$ and $\underline{J}^o_{m_i} = \rho x_i \underline{v}_i = M_i \underline{J}^o_{n_i}$. Equivalently,

$$\underline{J}^o_m = \rho \underline{v}_m = \sum_i \underline{J}^o_{m_i} = \sum_i \rho_i \underline{v}_{m_i} = \sum_i M_i \underline{J}^o_{n_i} = \sum_i M_i c_i \underline{v}_{n_i}$$

where $\rho_i = x_i \rho = M_i c_i$, $\rho = \sum_i \rho_i = \sum_i M_i c_i$.

Various extensive properties for a continuum

We say that property A is “extensive” if its instantaneous value for the material inside Σ_m can be written as

$$A(t) = \int_{\Sigma_m(t)} \rho\left(\underline{x},t\right)\; a^*(\underline{x},t)\,\mathrm{d}V$$

where $a^*(\underline{x},t)$ is the locally averaged specific property A per unit mass, taken from this table:

Extensive property	symbol A	per unit volume, ρa^*	per unit mass, a^*	Convective flux $\underline{J}^c_A = \underline{J}^o_A - \underline{J}_A$	Diffusive flux $\underline{J}_A$
Moles of i	n_i	c_i	c_i/ρ	$\underline{J}^c_{n_i} = c_i\,\underline{v}_m$	$\underline{J}_{n_i} = (\underline{v}_i - \underline{v}_m)c_i$
Total mole	n	$c = \sum_i c_i$	c/ρ	$\underline{J}^c_n = c\,\underline{v}_m$	$\underline{J}_n = \sum_i \underline{J}_{n_i}$
Mass of i	m_i	$\rho_i = M_i c_i$	x_i	$\underline{J}^c_{m_i} = M_i c_i\,\underline{v}_m$	$\underline{J}_{m_i} = M_i \underline{J}_{n_i}$
Total mass	m	$\rho = \sum_i \rho_i$	1	$\underline{J}^c_m = \rho\,\underline{v}_m$	$\underline{J}_m = \sum_i M_i \underline{J}_{n_i} = 0$
Charge of i	q_i	$\rho_{q_i} = F z_i c_i$	$F z_i c_i/\rho$	$\underline{J}^c_{q_i} = \rho_{q_i}\,\underline{v}_m$	$\underline{J}_{q_i} = F z_i \underline{J}_{n_i}$
Total charge	q	$\rho_q = \sum_i \rho_{q_i}$	ρ_q/ρ	$\underline{J}^c_q = \rho_q\,\underline{v}_m$	$\underline{J}_q = F \sum_i z_i \underline{J}_{n_i}$
Energy	E	ρe^*	e^*	$\underline{J}^c_E = \rho e^*\,\underline{v}_m$	$\underline{J}_E$
Entropy	S	ρs^*	s^*	$\underline{J}^c_S = \rho s^*\,\underline{v}_m$	$\underline{J}_S$
Kinetic energy	E_{kin}	ρv_m^2	v_m^2	$\underline{J}^c_{E_{\mathrm{kin}}} = \rho v_m^2\,\underline{v}_m$	$\underline{J}_{E_{\mathrm{kin}}}$
Potential energy (gravitational)	$E_{\mathrm{pot,g}}$	$\rho\varphi_g$	φ_g	$\underline{J}^c_{E_{\mathrm{pot,g}}} = \rho\varphi_g\,\underline{v}_m$	$\underline{J}_{E_{\mathrm{pot,g}}} = \varphi_g\,\underline{J}_m$
Potential energy (electrostatic)	$E_{\mathrm{pot,el}}$	$\rho_q\varphi$	$\rho_q\varphi/\rho$	$\underline{J}^c_{E_{\mathrm{pot,el}}} = \rho_q\varphi\,\underline{v}_m$	$\underline{J}_{E_{\mathrm{pot,el}}} = \varphi\,\underline{J}_q$
Momentum[‡]		$\rho\underline{v}_m$	$\underline{v}_m$	$\underline{J}^c_{\underline{v}_m} = \rho\underline{v}_m\,\underline{v}_m$	$\underline{J}_{\underline{v}_m} = \underline{\underline{P}} = -\underline{\underline{\tau}}$

[‡] **Note:** For simplicity, and to obtain the commonly accepted non-equilibrium thermodynamic results, we assume the momentum density to be given by $\rho\underline{v}_m$. However, note that following Brenner this is not generally correct, because we should define a momentum velocity $\underline{v}_{\mathrm{mom}}$ different from $\underline{v}_m$. To see how this would modify our subsequent non-equilibrium thermodynamic results, see D. Bedeaux, S. Kjelstrup, H.C. Öttinger, Physica A, Vol. 371, 177 (2006).

Nonequilibrium in heat, mass, and charge transfer

Continuum assumption

Local densities of the extensive properties from local-equilibrium (bulk-flow) assumptions

Continuum approximation vs Knudsen number

		Dry air at sea level	**at the Karman line (100km altitude)**	
Dry air		**25°C, 1 atm**	**-80°C, 0.01 atm**	
Avogadro's number	Nav	6.02214076E+26	6.02214076E+26	molecules/kmol
Boltzmann constant	$k_B=R/N_{AV}$	1.380649E-23	1.380649E-23	kJ/molecule K
Universal gas constant	$R=k_BN_{AV}$	8.31446E+03	8.31446E+03	kJ/kmol K
Temperature	T	298.15	193.15	K
Pressure	p	101.325	1	kPa
Molar concentration	[N]=n/V=p/RT	0.0000409	0.0000006	kmol/m^3
Number density	(n/V)*Nav	2.461E+22	3.750E+20	molecules/m^3
Mean interparticle distance	[(n/V)*Nav]$^{-1/3}$	3.44E-08	1.39E-07	m
Dynamic viscosity of air	μ	1.85E-05	1.30E-05	kg/m s
Molar mass	M	28.962	28.962	kg/kmol
Mean free path	λ=μ/p (π k_B T/2M)$^{1/2}$	6.70E-08	3.84E-06	m
Mean speed	w=(8RT/π M)$^{1/2}$	466.9	375.8	m/s
Collision frequency	Z=w/λ	6.97E+09	9.79E+07	1/s
Collisions per s in 1 m^3	z=Zp/2k_BT	8.57E+34	1.84E+31	1/s m^3
Mean interparticle distance	0.893(3k_BT/4 π p)$^{1/3}$	1.904E-09	7.682E-09	m

		Validity of continuum hypothesis requires Kn << 0.01							
	L	7cm	7mm	0.7mm	70μm	7μm	0.7μm	70nm	7nm
air at sea level	Kn=λ/L	1E-06	1E-05	1E-04	1E-03	1E-02	1E-01	1E+00	1E+01
air at the Karman line	Kn=λ/L	6E-05	6E-04	6E-03	6E-02	6E-01	6E+00	6E+01	6E+02

Ingredients of the general balance equations for the extensive properties of a continuum:

Gibbs-Duhem and local-equilibrium simple-system bulk-flow relations

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \textstyle\sum_i \mu_i\,\mathrm{d}n_i$$ **Gibbs relation**

$$U - TS + pV - \textstyle\sum_i \mu_i\, n_i = \begin{cases} 0 & \text{for large } n \\ \mathit{Eu} \neq 0 & \text{for small } n \end{cases}$$ **Euler relation**

$$-\,S\,\mathrm{d}T + V\,\mathrm{d}p - \textstyle\sum_i n_i\,\mathrm{d}\mu_i = \begin{cases} 0 & \text{for large } n \\ \mathrm{d}\mathit{Eu} \neq 0 & \text{for small } n \end{cases}$$ **Gibbs-Duhem relation**

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,\boldsymbol{n}_i'} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\boldsymbol{n}_i'}$$

$$\mathrm{d}\mu_i = \underbrace{\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}}}_{-s_i}\mathrm{d}T + \underbrace{\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}}}_{v_i}\mathrm{d}p + \sum_{j=1}^{r}\underbrace{\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}_j'}}_{\mu_{i,j}\,=\,\mu_{i,j}}\mathrm{d}n_j = -s_i\,\mathrm{d}T + \boxed{\underbrace{v_i\,\mathrm{d}p + \textstyle\sum_{j=1}^{r}\mu_{i,j}\,\mathrm{d}n_j}_{\mathrm{d}\mu_i|_T}}$$

$$E = U(S,V,\boldsymbol{n}) + \tfrac{1}{2}m v_m^2 + mgz + q\varphi - \tfrac{1}{2}m\omega^2\mathrm{r}^2 \qquad m = \textstyle\sum_i n_i M_i \qquad q = \textstyle\sum_i n_i z_i F$$

$$\mathrm{d}E = \mathrm{d}U + \tfrac{1}{2}v_m^2\,\mathrm{d}m + m v_m\,\mathrm{d}v_m + gz\,\mathrm{d}m + mg\,\mathrm{d}z + \varphi\,\mathrm{d}q + q\,\mathrm{d}\varphi - \tfrac{1}{2}\omega^2\mathrm{r}^2\,\mathrm{d}m - m\omega\mathrm{r}^2\,\mathrm{d}\omega - m\omega^2\mathrm{r}\,\mathrm{d}\mathrm{r}$$

$$\mu_i^{\mathrm{tot}} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,\boldsymbol{n}_i',v_m,z,\varphi,\omega,\mathrm{r}} = \mu_i + \tfrac{1}{2}M_i v_m^2 + M_i g z + z_i F\,\varphi - \tfrac{1}{2}M_i\omega^2\mathrm{r}^2$$

$$U = nu = mu^* = V\rho u^* = Vcu, \quad u = \textstyle\sum_i y_i u_i + \left(\mathit{eu} - T\,\mathit{eu}_{,T} - p\,\mathit{eu}_{,p}\right) \quad v = \textstyle\sum_i y_i v_i + \left(\mathit{eu}_{,p}\right)$$

$$S = ns = ms^* = V\rho s^* = Vcs, \quad s = \textstyle\sum_i y_i s_i - \left(\mathit{eu}_{,T}\right), \quad \mathit{Eu} = n\,\mathit{eu} = m\,\mathit{eu}^* = V\rho\,\mathit{eu}^* = Vc\,\mathit{eu}$$

$$\rho = \frac{m}{V}, c = \frac{n}{V}, y_i = \frac{n_i}{n}, c_i = \frac{n_i}{V}, x_i\frac{m_i}{m}, m_i = n_i M_i, m = \textstyle\sum_i m_i, n = \textstyle\sum_i n_i, \mu_i^* = \frac{\mu_i}{M_i}, \mu_i^{*\mathrm{tot}} = \frac{\mu_i^{\mathrm{tot}}}{M_i}$$

Ingredients of the general balance equations for the extensive properties of a continuum:

Gibbs-Duhem relation in terms of molar and mass specific properties

In terms of **molar specific** properties

$$\mathrm{d}u = T\,\mathrm{d}s - p\,\mathrm{d}v + \textstyle\sum_i \mu_i\,\mathrm{d}y_i - \begin{cases} 0 & \text{for large } n \\ e\!\!u\frac{\mathrm{d}n}{n} \neq 0 & \text{for small } n \end{cases}$$

Gibbs relation

$$u - Ts + pv - \textstyle\sum_i \mu_i\, y_i = \begin{cases} 0 & \text{for large } n \\ e\!\!u \neq 0 & \text{for small } n \end{cases}$$

Euler relation

$$-\,s\,\mathrm{d}T + v\,\mathrm{d}p - \textstyle\sum_i y_i\,\mathrm{d}\mu_i = \begin{cases} 0 & \text{for large } n \\ \mathrm{d}e\!\!u + e\!\!u\,\frac{\mathrm{d}n}{n} \neq 0 & \text{for small } n \end{cases}$$

Gibbs-Duhem relation

$$v\,\mathrm{d}p - \textstyle\sum_i y_i\,\mathrm{d}\mu_i|_T = \begin{cases} 0 & \text{for large } n \\ \mathrm{d}e\!\!u + e\!\!u\,\frac{\mathrm{d}n}{n} - e\!\!u_{,T}\,\mathrm{d}T \neq 0 & \text{for small } n \end{cases} \Rightarrow v\,\nabla p = \textstyle\sum_i y_i\,\nabla\mu_i|_T$$

In terms of **mass specific** properties

$$\mathrm{d}u^* = T\,\mathrm{d}s^* + \frac{p}{\rho^2}\,\mathrm{d}\rho + \textstyle\sum_i \mu_i^*\,\mathrm{d}x_i - \begin{cases} 0 & \text{for large } n \\ e\!\!u^*\frac{\mathrm{d}m}{m} \neq 0 & \text{for small } n \end{cases}$$

Gibbs relation

$$u^* - Ts^* + pv^* - \textstyle\sum_i \mu_i^*\, x_i = \begin{cases} 0 & \text{for large } n \\ e\!\!u^* \neq 0 & \text{for small } n \end{cases}$$

Euler relation

$$-\,s^*\,\mathrm{d}T + \frac{1}{\rho}\,\mathrm{d}p - \textstyle\sum_i x_i\,\mathrm{d}\mu_i^* = \begin{cases} 0 & \text{for large } n \\ \mathrm{d}e\!\!u^* + e\!\!u^*\,\frac{\mathrm{d}m}{m} \neq 0 & \text{for small } n \end{cases}$$

Gibbs-Duhem relation

$$\mathrm{d}p - \rho\textstyle\sum_i x_i\,\mathrm{d}\mu_i^*|_T = \begin{cases} 0 & \text{for large } n \\ \rho\,\mathrm{d}e\!\!u^* + \rho\,e\!\!u^*\,\frac{\mathrm{d}m}{m} - \rho\,e\!\!u^*_{,T}\,\mathrm{d}T \neq 0 & \text{for small } n \end{cases} \Rightarrow \nabla p = \rho\textstyle\sum_i x_i\,\nabla\mu_i^*|_T$$

Ingredients of the general balance equations for the extensive properties of a continuum:

Gibbs and Gibbs-Duhem relation in terms of volume specific properties

In terms of **volume specific** properties, the pressure disappears from the Gibbs relation

$$\left.\begin{aligned} \mathrm{d}(\rho u^*) &= T\,\mathrm{d}(\rho s^*) \\ \mathrm{d}(cu) &= T\,\mathrm{d}(cs) \end{aligned}\right\} + \textstyle\sum_i \mu_i\,\mathrm{d}c_i - \begin{cases} 0 & \text{for large } n \\ c\,eu\frac{\mathrm{d}V}{V} \neq 0 & \text{for small } n \end{cases} \Rightarrow \frac{\partial \rho u^*}{\partial t} = T\,\frac{\partial \rho s^*}{\partial t} + \textstyle\sum_i \mu_i\,\frac{\partial c_i}{\partial t}$$

Gibbs relation

$$\left.\begin{aligned} (\rho u^*) &= T\,(\rho s^*) \\ (cu) &= T\,(cs) \end{aligned}\right\} + p - \textstyle\sum_i \mu_i\,c_i = \begin{cases} 0 & \text{for large } n \\ c\,eu \neq 0 & \text{for small } n \end{cases}$$

Euler relation

$$\left.\begin{aligned} -(\rho s^*)\,\mathrm{d}T \\ -(cs)\,\mathrm{d}T \end{aligned}\right\} + \mathrm{d}p - \textstyle\sum_i c_i\,\mathrm{d}\mu_i = \begin{cases} 0 & \text{for large } n \\ c\,\mathrm{d}eu + c\,eu\,\frac{\mathrm{d}V}{V} \neq 0 & \text{for small } n \end{cases}$$

Gibbs-Duhem relation

$$\mathrm{d}p - \textstyle\sum_i c_i\,\mathrm{d}\mu_i|_T = \begin{cases} 0 & \text{for large } n \\ c\,\mathrm{d}eu + c\,eu\,\frac{\mathrm{d}V}{V} - c\,eu_{,T}\,\mathrm{d}T \neq 0 & \text{for small } n \end{cases} \Rightarrow \nabla p = \textstyle\sum_i c_i\,\nabla \mu_i|_T$$

Where, remember,

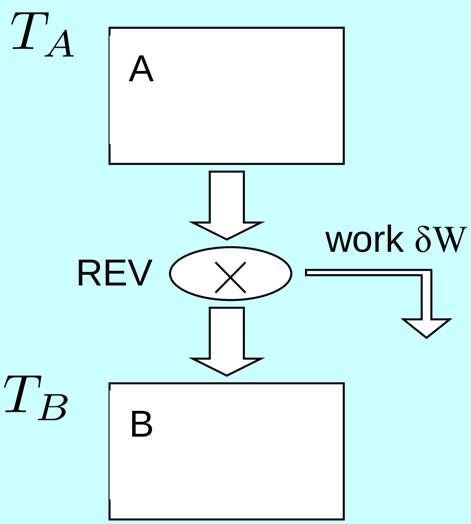
$$\mathrm{d}\mu_i = \underbrace{\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}}}_{-s_i}\mathrm{d}T + \underbrace{\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}}}_{v_i}\mathrm{d}p + \sum_{j=1}^{r}\underbrace{\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j}}_{\mu_{i,j}\,=\,\mu_{i,j}}\mathrm{d}n_j = -s_i\,\mathrm{d}T + \underbrace{v_i\,\mathrm{d}p + \textstyle\sum_{j=1}^{r}\mu_{i,j}\,\mathrm{d}n_j}_{\mathrm{d}\mu_i|_T}$$

Nonequilibrium in heat, mass, and charge transfer

Generalizations of the concept of heat interaction: “heat&diffusion” interaction

Recall how we defined "heat interactions"...

A and B fixed n and V



$$dE^A = -\delta E^{A\to B}$$

$$dS^A = -\delta S^{A\to B}$$

Gibbs relation for A

$$dE^A = T_A\, dS^A$$

$$dE^B = \delta E^{A\to B} - \delta W$$

$$dS^B = \delta S^{A\to B}$$

Gibbs relation for B

$$dE^B = T_B\, dS^B$$

Energy balance $dE^A + dE^B = -\delta W$

Entropy balance $dS^A + dS^B = \delta S_{\text{gen}} = 0$ to have max δW

$$\boxed{\delta W = \delta E^{A\to B}\left(1 - \frac{T_B}{T_A}\right)}$$

... and proved the Clausius statement of the second law

A and B fixed n and V

$$\boxed{\delta W = \delta E^{A\to B}\left(1 - \frac{T_B}{T_A}\right)}$$

$$\frac{\delta W}{\delta E^{A\to B}} \to 0 \qquad\qquad T_A = T_B = T$$

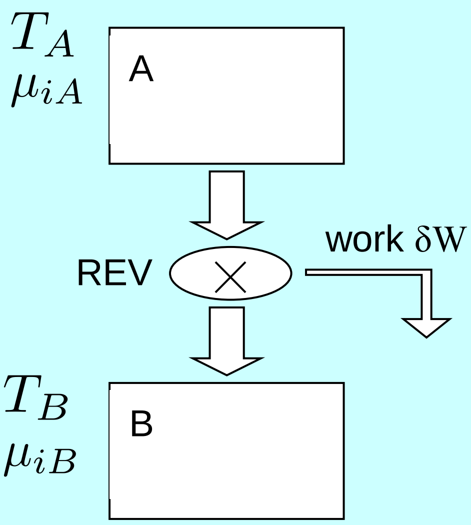
$$\boxed{\frac{\delta E^{A\to B}}{T^A} \le \delta S^{A\to B} \le \frac{\delta E^{A\to B}}{T^B}}$$

$$\left.T_A = T_B = T \right\} \quad \boxed{\delta E^{A\to B} = T\,\delta S^{A\to B}}$$

$$\left.\begin{aligned} J_E &= \frac{\delta E^{A\to B}}{\mathrm{d}t\,A} \\ J_S &= \frac{\delta S^{A\to B}}{\mathrm{d}t\,A} \end{aligned}\right\} \quad \boxed{J_E = T\,J_S}$$

Use the same logic to define "heat&diffusion interactions"...

A and B fixed V



$$dE^A = -\delta E^{A\to B}$$

$$dS^A = -\delta S^{A\to B}$$

$$dn_i^A = -\delta n_i^{A\to B}$$

$$dE^B = \delta E^{A\to B} - \delta W$$

$$dS^B = \delta S^{A\to B}$$

$$dn_i^B = \delta n_i^{A\to B}$$

Gibbs relation for A

$$dE^A = T_A\, dS^A + \sum_i \mu_{iA}\, dn_i^A$$

Gibbs relation for B

$$dE^B = T_B\, dS^B + \sum_i \mu_{iB}\, dn_i^B$$

Energy balance $dE^A + dE^B = -\delta W$

Balance of constituent i $dn_i^A + dn_i^B = 0$

Entropy balance $dS^A + dS^B = \delta S_{\text{gen}} = 0$ to have max δW

$$\delta W = \delta E^{A\to B}\left(1 - \frac{T_B}{T_A}\right) + \sum_i \delta n_i^{A\to B}\left(\mu_{iA}\frac{T_B}{T_A} - \mu_{iB}\right)$$

... and generalize the Clausius statement of the second law

A and B fixed V

$$\delta W = \delta E^{A\to B}\left(1-\frac{T_B}{T_A}\right)+\sum_i \delta n_i^{A\to B}\left(\mu_{iA}\frac{T_B}{T_A}-\mu_{iB}\right)$$

$$\frac{\delta W}{\delta E^{A\to B}}\to 0 \quad \text{and} \quad \frac{\delta W}{\delta n_i^{A\to B}}\to 0 \qquad T_A = T_B = T \qquad \mu_{iA}=\mu_{iB}=\mu_i$$

$$\frac{\delta E^{A\to B}-\sum_i \mu_{iA}\,\delta n_i^{A\to B}}{T^A} \le \delta S^{A\to B} \le \frac{\delta E^{A\to B}-\sum_i \mu_{iB}\,\delta n_i^{A\to B}}{T^B}$$

$$\left.\begin{aligned} T_A &= T_B = T \\ \mu_{iA} &= \mu_{iB} = \mu_i \end{aligned}\right\} \qquad \delta E^{A\to B} = T\,\delta S^{A\to B} + \sum_i \mu_i\,\delta n_i^{A\to B}$$

$$\left.\begin{aligned} J_E &= \frac{\delta E^{A\to B}}{\mathrm{d}t\,A} \\ J_S &= \frac{\delta S^{A\to B}}{\mathrm{d}t\,A} \\ J_{n_j} &= \frac{\delta n_j^{A\to B}}{\mathrm{d}t\,A} \end{aligned}\right\} \qquad J_E = T\,J_S + \sum_i \mu_i\,J_{n_i}$$

Only a fraction of $\mathbf{J}_E$ is $\mathbf{q}''$ in a "heat&diffusion" interaction

$$\delta E^{A\to B} = T\delta S^{A\to B} + \sum_i \mu_i \delta n_i^{A\to B}$$

$$\mathbf{J}_E = T\mathbf{J}_S + \sum_i \mu_i \mathbf{J}_{n_i}$$

Using $\mu_i = h_i - Ts_i$ rewrite as $\mathbf{q}'' = \mathbf{J}_E - \sum_i h_i \mathbf{J}_{n_i} = T\left(\mathbf{J}_s - \sum_i s_i \mathbf{J}_{n_i}\right)$

Therefore, we define the (measurable*) heat flux $\mathbf{q}''$ so that

$$\mathbf{J}_E = \mathbf{q}'' + \sum_i h_i \mathbf{J}_{n_i}$$

$$\mathbf{J}_S = \frac{\mathbf{q}''}{T} + \sum_i s_i \mathbf{J}_{n_i}$$

Partial enthalpy

$$h_i = \left(\frac{\partial\left(\mu_i/T\right)}{\partial\left(1/T\right)}\right)_{p,\mathbf{n}}$$

Partial entropy

$$s_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\mathbf{n}}$$

*De Groot & Mazur call $\mathbf{q}''$ the **measurable heat flux**, but denote it by $\mathbf{J}'_q$ (please note that their use of the prime differs from our use here).

Only a fraction of J_E is q″ in a “heat&diffusion” interaction

If constituents carry electric charge $\mu_i \to \mu_{i,\mathrm{tot}} = \mu_i + z_i F \varphi$

$$\mathbf{J}_E = T\mathbf{J}_S + \sum_i \mu_i \mathbf{J}_{n_i} \to \mathbf{J}_E = T\mathbf{J}_S + \sum_i \mu_{i,\mathrm{tot}} \mathbf{J}_{n_i} = T\mathbf{J}_S + \sum_i \mu_i \mathbf{J}_{n_i} + \varphi \mathbf{I}''$$

Use $\mu_i = h_i - T s_i$ and (*) $\mathbf{I}'' = F \sum_i z_i \mathbf{J}_{n_i}$

rewrite as $\mathbf{q}'' = \mathbf{J}_E - \sum_i h_i \mathbf{J}_{n_i} - \varphi \mathbf{I}'' = T\left(\mathbf{J}_S - \sum_i s_i \mathbf{J}_{n_i}\right)$

Therefore, we define the (measurable*) heat flux $\mathbf{q}''$ so that

$$\mathbf{J}_E = \mathbf{q}'' + \sum_i h_i \mathbf{J}_{n_i} + \varphi \mathbf{I}''$$

$$\mathbf{J}_S = \frac{\mathbf{q}''}{T} + \sum_i s_i \mathbf{J}_{n_i}$$

(*) Partial charge flux due to the diffusion of component i: $\mathbf{I}''_i = z_i F \mathbf{J}_{n_i}$

(*) Total charge flux (current density):

$$\mathbf{I}'' = \sum_i \mathbf{I}''_i = \sum_i z_i F \mathbf{J}_{n_i}$$

*De Groot & Mazur call $\mathbf{q}''$ the **measurable heat flux**, but denote it by $\mathbf{J}'_q$ (please note that their use of the prime differs from our use here).

“Heat&diffusion” mode of interaction between adjacent elements

The energy, entropy, and mole fluxes are related by

$$\underline{J}_S = \tau\,\underline{J}_E^{\rm nw} + \textstyle\sum_i \lambda_i^{\rm tot}\,\underline{J}_{n_i} \qquad \text{recall:} \quad \tau = \frac{1}{T} \quad \text{and} \quad \lambda_i^{\rm tot} = -\frac{\mu_i^{\rm tot}}{T}$$

and, therefore, the divergences of the fluxes are related by

$$\underline{\nabla}\cdot\underline{J}_S = \underline{\nabla}\tau\cdot\underline{J}_E^{\rm nw} + \tau\underline{\nabla}\cdot\underline{J}_E^{\rm nw} + \textstyle\sum_i \underline{\nabla}\lambda_i^{\rm tot}\cdot\underline{J}_{n_i} + \textstyle\sum_i \lambda_i^{\rm tot}\underline{\nabla}\cdot\underline{J}_{n_i}$$

The mass specific energy of the fluid element at $(\boldsymbol{x}, t)$ may be written as

$$e^* = u^*(\rho s^*, \boldsymbol{c}) + \tfrac{1}{2}v_m^2 + gz + \rho_q\varphi/\rho$$

$$\rho e^* = \rho\, u^*(\rho s^*, \boldsymbol{c}) + \textstyle\sum_i c_i \left(\tfrac{1}{2}M_i v_m^2 + M_i g z + z_i F \varphi\right)$$

where $u^* = u^*(\rho s^*, \boldsymbol{c})$ is the stable-equilibrium simple-system fundamental relation expressing the specific energy for a surrogate fluid element with the same entropy density and molar densities but viewed from a reference frame moving with the barycentric velocity $\underline{v}_m$ and with the chemical reactions and the gravitational and electrostatic fields turned off. Recalling that the natural variables of the chemical potential μ_i are $T, p, \boldsymbol{y}$, the total potentials, therefore, are

$$\mu_i^{\rm tot} = \mu_i(T, p, \boldsymbol{y}) + \tfrac{1}{2}M_i v_m^2 + M_i g z + z_i F \varphi$$

which results when E is assumed to be a function of S, V, $\underline{n}$, $\frac{1}{2}v_m^2$, gz, and φ, and the total potential is defined as

$$\mu_i^{\rm tot} = \left(\frac{\partial E}{\partial n_i}\right)_{S,\,V,\,\underline{n}',\,v_m,\,z,\,\varphi} = \left(\frac{\partial(\rho e^*)}{\partial c_i}\right)_{s,\,\underline{c}',\,v_m,\,z,\,\varphi}$$

where the second equality follows from observing that $({\rm d}E)_V = V\,{\rm d}(\rho e^*)$, $({\rm d}S)_V = V\,{\rm d}(\rho s^*)$, and $({\rm d}n_i)_V = V\,{\rm d}c_i$.

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