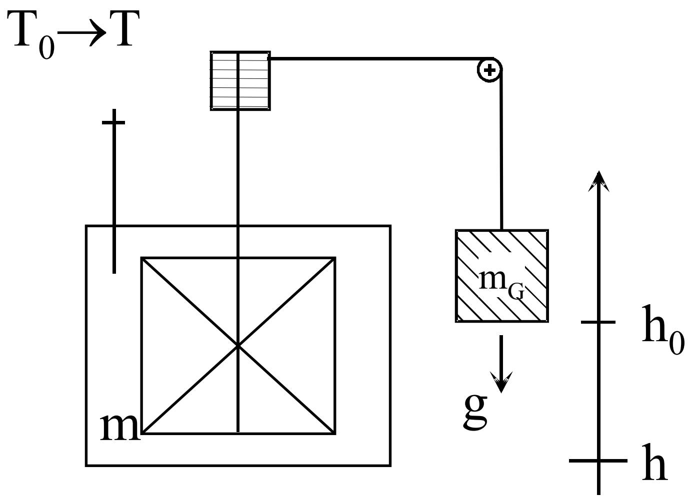
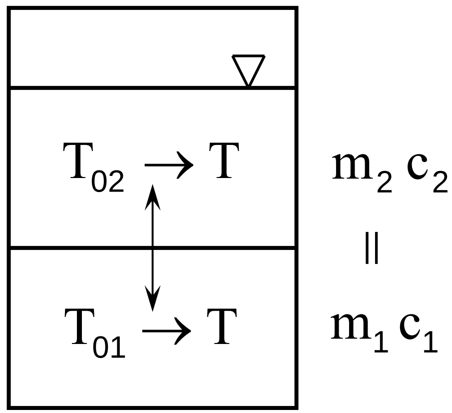
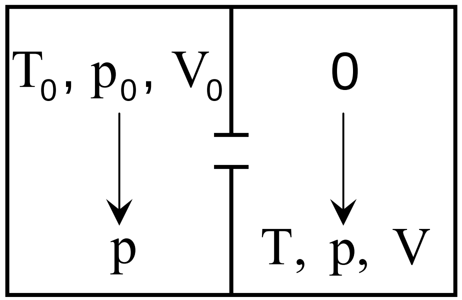
Irreversibility of Processes in Closed System







J.P. Joule
Stirring experiment

J.B. Fourier
Heat transfer

Gay-Lussac
Gas expansion

$$m_G g(h_0 - h) = m c_v (T - T_0) \gtrless 0$$

$$T_{01} - T = T - T_{02} \gtrless 0$$

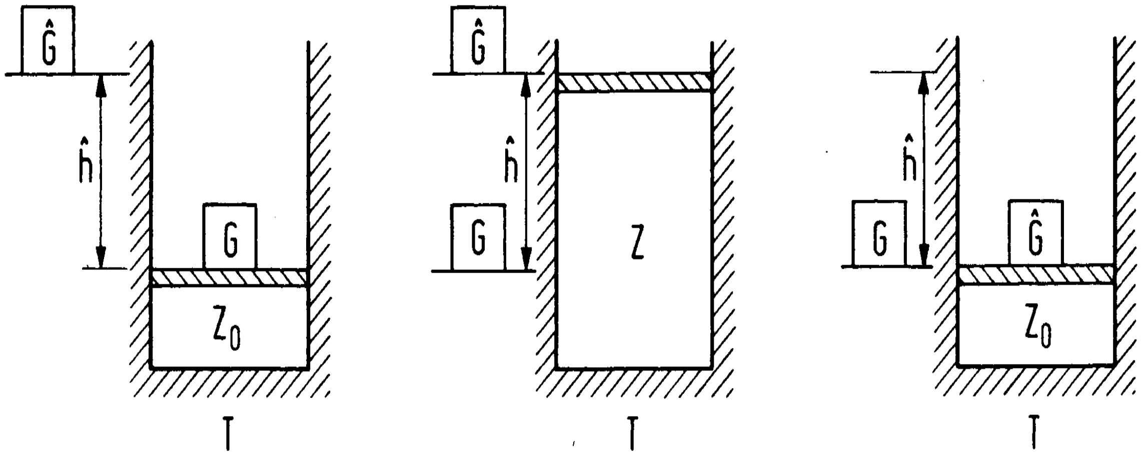
$$U(T_0, V_0, m) = U(T, V_0 + V, m)$$

$$V \gtrless 0$$

$$\text{I.G.}: T_0 = T$$

Gas Expansion Process

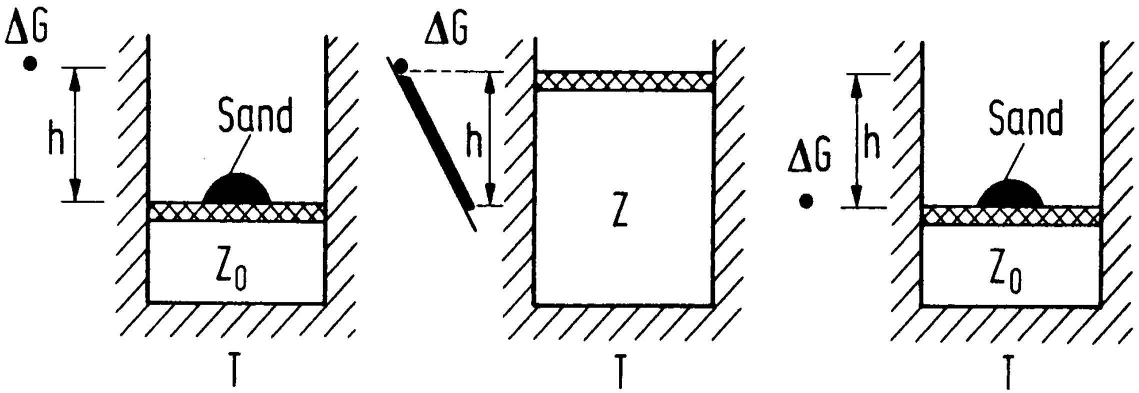
Irreversibility



VELO	> 0
Z	NEQ
Σ*’	≠ Σ*
REV	F > 0

Reversibility

VELO	~~0~~
Z	EQ
Σ*’	= Σ*
REV	F = 0

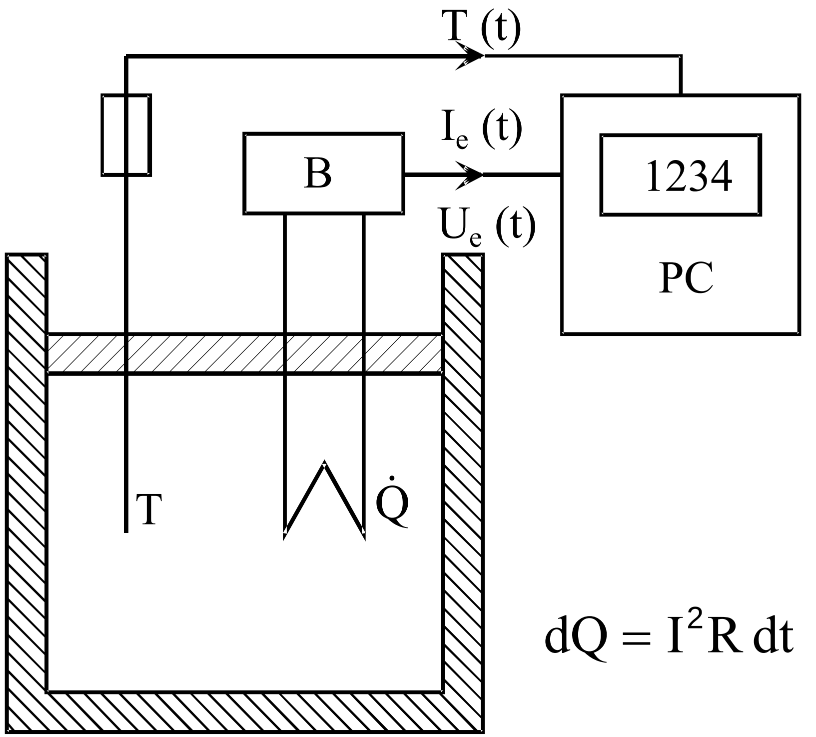


2^{nd} Law (1): Clausius Entropy

$$S(Z) = S(Z_0) + \oint_{Z_0}^{Z} \frac{dQ_{rev}}{T} \quad \dots \quad dT \to 0$$

Clausius Equality $(Z = Z_0)$

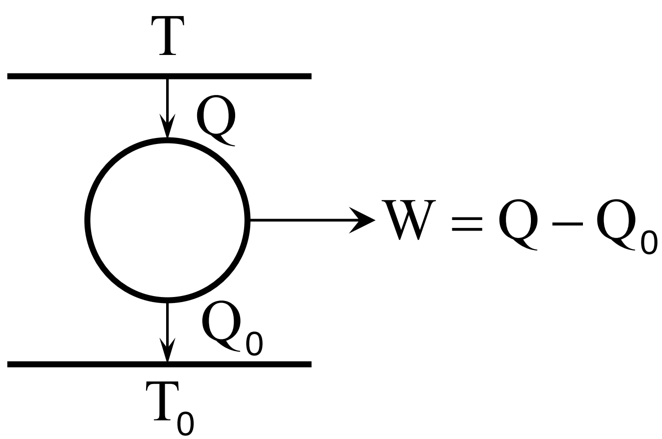
$$0 = \oint \frac{dQ_{rev}}{T}$$



Entropymeter

Carnot-Relation

$$\frac{Q}{T} = \frac{Q_0}{T_0} \quad , \quad \eta_c = \frac{W}{Q} = 1 - \frac{T_0}{T}$$

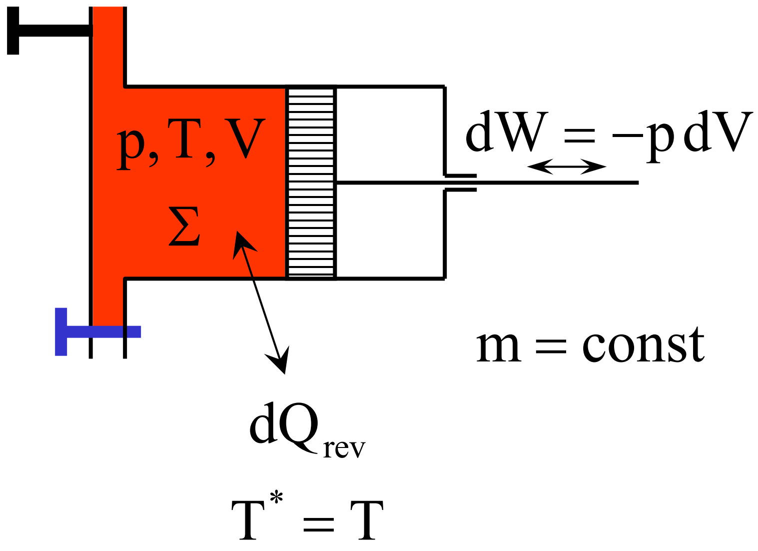


Gibbs Equation (Simple System)

1^{st} Law : $$dU = dQ_{rev} - p\,dV$$

2^{nd} Law: $$dS = dQ_{rev}/T$$

Gibbs: $$dS = \frac{1}{T}dU + \frac{p}{T}dV$$



$$\left(\frac{\partial^2 S}{\partial T\,\partial V}\right) = \left(\frac{\partial^2 S}{\partial V\,\partial T}\right) \rightarrow S = S_0 + \int_{T_0(V_0)}^{T} \frac{C_{V_0}}{T'}dT' + \int_{V_0(T)}^{V}\left[\frac{\partial p(T,V')}{\partial T}\right]_T dV'$$

Caloric EOS Thermal EOS

Entropy of Ideal Substances

Ideal Gas

TEOS: $pV = (m/M)RT$

CEOS: $H = H_0 + mc_p(T - T_0)$

$$\rightarrow S = S_0 + m\left[c_p \ln\left(\frac{T}{T_0}\right) - \frac{R}{M}\ln\left(\frac{p}{p_0}\right)\right]$$

$$\rightarrow S = S_0 + m\left[c_v \ln\left(\frac{T}{T_0}\right) + \frac{R}{M}\ln\left(\frac{V}{V_0}\right)\right]$$

Ideal Liquid

TEOS: $\rho = \text{const} = 1/v$

CEOS: $c = \text{const}$

$$H = H_0 + mc(T - T_0) + mv(p - p_0)$$

$$S = S_0 + mc\ln\left(\frac{T}{T_0}\right)$$

$$S(U,n_1...n_N) = S^* + \sum_{i=1}^{N} c_{i0} \ln\left(1 + \frac{U-U^*}{cnT^*}\right) n_i$$

$$S(U^*,n_1...n_N) \equiv S^* = \sum_{i=1}^{N} (s_{i0}^* - R\ln x_i) n_i$$

$$G(T,n_1...n_N) = G^* + \sum_{i=1}^{N} \left[(c_{i0} - s_{i0}^* + R\ln x_i)(T-T^*) - c_{10} T \ln\left(\frac{T}{T^*}\right)\right] n_i$$

$$G(T^*,n_1...n_N) \equiv G^* = \sum_{i=1}^{N} (-s_{i0}^* + R\ln x_i) T^* n_i + U^* + pV$$

$$U = \sum_i U_{i0} = U^* + \sum_{i=1}^{N} c_{i0}(T-T^*) n_i \;,\; V = \sum_{i=1}^{N} v_{i0} n_i$$

$$H = \sum_i H_{i0} = H^* + \sum_{i=1}^{N} \left[c_{i0}(T-T^*) + pv_{i0}\right] n_i$$

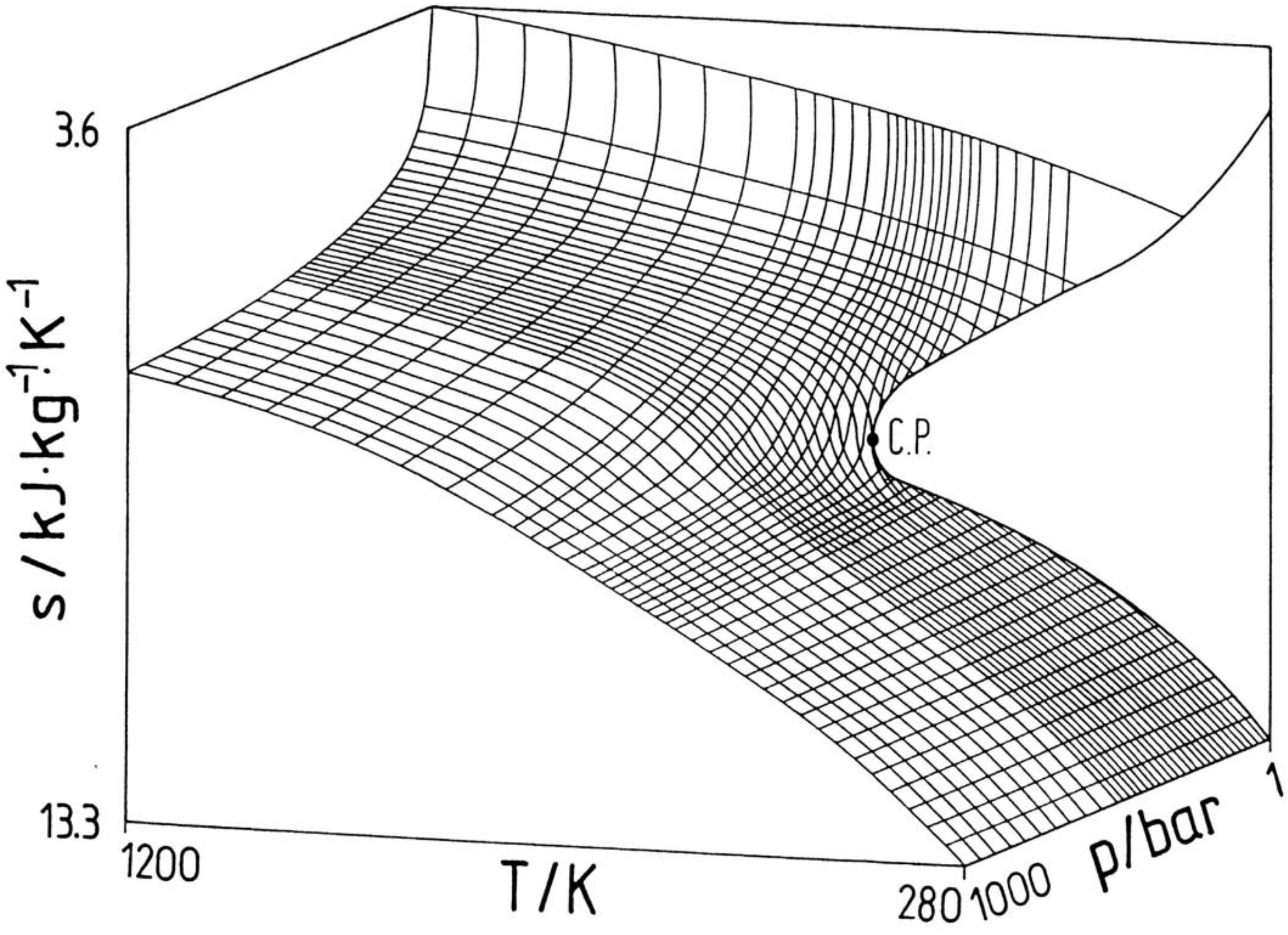
$$\mu_i(T,n_1...n_N) = \mu_i^* + (T-T^*) s_{i0}^* + c_{i0} T \ln\left(\frac{T}{T^*}\right) - R(T-T^*)\ln x_i$$

$$\mu_i(T^*,n_1...n_N) \equiv \mu_i^* = T^* s_{i0}^* - RT^* \ln x_i$$

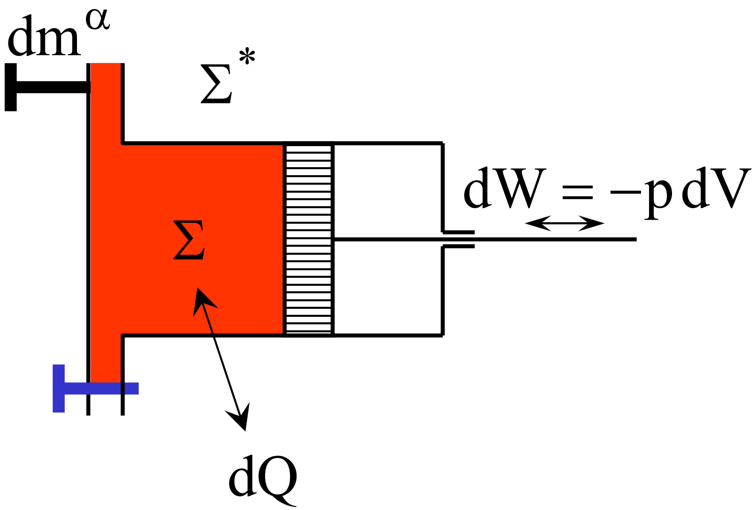
Incompressible, ideal fluid mixture $(c_{i0} = \text{const}, v_{i0} = \text{const}, i = 1...N)$

Entropy of Water (H_2O)

K. Stephan, W. Wagner
IAPS (1985)



2nd Law (2): Clausius Inequality



Exchange of
mass heat work

$$\Sigma: \quad Z_0 \to Z$$

IRR :
REV :

$$S - S_0 \geq \oint_{Z_0}^{Z} \left(\frac{dQ}{T^*} + \sum_{\alpha} s^{(\alpha)} dm^{(\alpha)} \right)$$

Quasistatic changes of state ($Z \to Z + dZ$)

$$dS \geq \frac{dQ}{T^*} + \sum_{\alpha=1}^{A} s^{(\alpha)} dn^{(\alpha)}$$

Closed Systems: $dQ = 0 \,, \; dm^{(\alpha)} = 0$

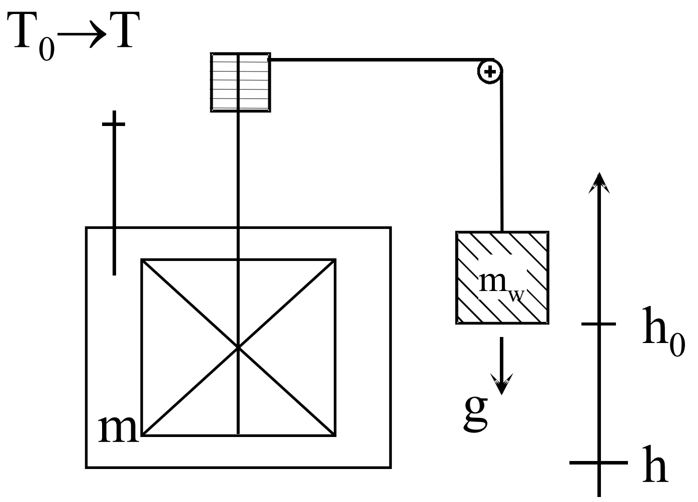
IRR :
REV :

$S \geq S$ ... World Statement?

Interpretations of the Clausius Entropy (S(Z))

1. M. Planck (1885)
   Measure for “probability”, tendency, preference of a system to actually realize a certain equilibrium state (Z).
   (N_2-gas in steel bottle)
2. L. Boltzmann (1890)
   Measure for molecular “disorder” in a system in state (Z).
   (Crystal, liquid, gas, plasma ...)
3. C. Shannon (1948)
   Measure for “lack of knowledge” of the micro- i.e. molecular state of a system (Σ) in a given macroscopic state (Z)

Stirring Experiment of J.P Joule



1st Law: $U_0 + m_w g h_0 = U + m_w g h$

CEOS: $U = U_0 + m c_v (T - T_0)$

2nd Law (1), I.G.: $S = S_0 + m c_v \ln\left(\frac{T}{T_0}\right)$

$Z_0 : T_0, h_0$

$Z : T, h$

$Z_0 \rightarrow Z$

2nd Law (2): $S > S_0$

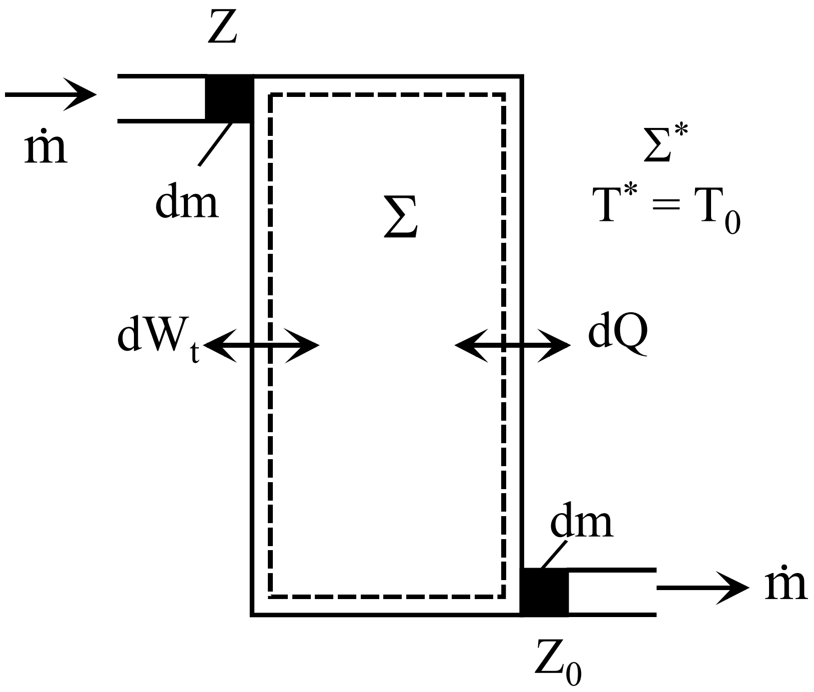
$\rightarrow T > T_0$

$\rightarrow h < h_0$

Reversed process $(T < T_0, h > h_0)$ not possible!

Maximum Work of a Mass Flow (H. von Helmholtz (1890))

Simple open system $(Z \to Z_0)$



$Z: \quad h, s, T, p, \rho$

$Z_0: \quad h_0, s_0, T_0 = T^*, p_0, \rho_0$

Stationary State $(\dot{Z} = 0)$

1st Law : $\dot{U} = \dot{Q} + \dot{W}_t + (h - h_0)\dot{m} = 0$

2nd Law: $\dot{S} = \dfrac{\dot{Q}}{T^*} + (s - s_0)\dot{m} + P_s = 0$

$$P_s \geq 0$$

$$-\dot{W}_t = \left[h - h_0 - T^*(s - s_0)\right]\dot{m} - T^* P_s$$

$$-\dot{W}_t = e_x(Z, Z_0)\dot{m} + P_{ex}$$

$$P_{ex} = -T^* P_s \leq 0$$

Thermodynamics of Processes (1)

Discrete System, Exchange of Heat, Work, Mass

Balance Equations :

$$\dot{n}_i = \sum_{\alpha} \dot{n}_i^{(\alpha)}$$

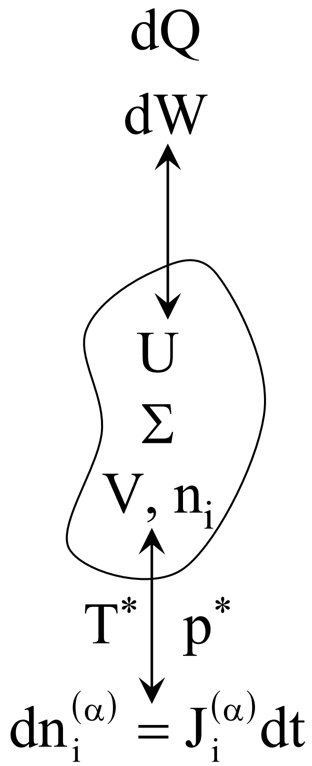
$$\dot{U} = \dot{Q} - p^* \dot{V} + \sum_{\alpha}^{A} h^{(\alpha)} \dot{n}^{(\alpha)}$$

Gibbs Equation :

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_{i}^{N} \mu_i dn_i$$

Clausius Inequality :

$$S - S_0 = \int_{Z_0}^{Z} \left(\frac{dQ}{T^*} + \sum_{\alpha} s^{(\alpha)} dn^{(\alpha)} \right)$$



Fundamental Inequality:

$$(*) \quad \int_0^t \left[\left(\frac{1}{T} - \frac{1}{T_*} \right) \dot{U} + \left(\frac{p}{T} - \frac{p^*}{T^*} \right) \dot{V} + \sum_{i,\alpha}^{N,A} \left(\frac{\mu_i^{(\alpha)}}{T^{(\alpha)}} - \frac{\mu_i}{T} \right) \dot{n}_i^{(\alpha)} \right] dt \geq 0 \; \ldots \text{ all } (t)$$

Thermal energy work mass exchange

Process Equations (Flux-Force-Relations)

(Eckart – Onsager – Meixner – Prigogine)

Thermal energy $\dot{U}(t) = F_u(\%)$

Heat transfer

Mechanical work $\dot{V}(t) = F_v(\%)$

Mass transfer $\underline{\dot{n}_i^{(\alpha)}(t) = F_i^{(\alpha)}(\%)}$ $i = 1 \ldots N$, $\alpha = 1 \ldots A$

$$(\%) = \left(\frac{1}{T} - \frac{1}{T^*}, \frac{p}{T} - \frac{p^*}{T^*}, \frac{\mu_k^{(\alpha)}}{T^{(\alpha)}} - \frac{\mu_k}{T}, k = 1 \ldots N, \alpha = 1 \ldots A \right)$$

F ... Functions or Functionals $(-\infty \le s \le t)$ of their arguments

Classification of Process Equations

F(%)		Linearity	Non-Linearity
	Function (t)	TIP	NTIP
	Functional (-∞<s≤t)	LPS	NPS (?)

Fundamental Inequality $\left(2^{nd}\text{ Law, }(*)\right)$
Theorem (JUK, 1968)

$$\int_0^t \sum_i^N \dot{x}_i F_i\left(\underline{x}, \underline{\dot{x}}\right) dt \geq 0 \text{ ... all } t \geq 0$$

$$F_i\left(\underline{x}, \underline{\dot{x}} = 0\right) = 0 \text{ , } i = 1 \ldots N$$

$$\rightarrow P_s = \sum_i^N \dot{x}_i F_i\left(\underline{x}, \underline{\dot{x}}\right) \geq 0$$

TIP

$$F_i\left(\underline{x}, \underline{\dot{x}}\right) = \sum_k^N L_{ik}\left(\underline{x}\right) \dot{x}_k$$

Onsager-Casimir-Relations

$$L_{ik} = \varepsilon_i \varepsilon_k L_{ki} \text{ , } \varepsilon_i, \varepsilon_k = \pm 1$$

NTIP

$$F_i\left(\underline{x}, \underline{\dot{x}}\right) = \sum_k^N L_{ik}\left(\underline{x}\right) \dot{x}_k + \sum_{klm} M_{iklm}\left(\underline{x}\right) \dot{x}_k \dot{x}_l \dot{x}_m + 0 \quad (5)$$

LPS

$F_i\left(\underline{x}, \underline{\dot{x}}\right)$ ... Linear Passive Functional
(J. Meixner, H. König, 1964)

Dimensional Analysis
Phenomenological Coefficients and Functions:

Buckingham's Theorem (π – Theorem):

$$Y = Y(Z_1 \ldots Z_M)$$

Basic Units System (SI-System)

$$G_1, G_2, \ldots G_g$$

$$\rightarrow \; Y = \prod_{i=1}^{M} Z_i^{\alpha_i} \phi(\pi_1 \ldots \pi_{M-r})$$

$$[Y] = \left[\prod_{i=1}^{M} Z_i^{\alpha_i} \right]$$

$$\pi_k = \prod_{j=1}^{M} Z_j^{\beta jk} \quad , \quad [\pi_k] = 1$$

$$\ln \phi = \phi_0 + \sum_{i=1}^{\mu - r} \phi_{1i} \ln \pi_i + \ldots$$

Dimensional Matrix

	Z_1	. . . . .	Z_M
G_1	ζ_{11}	. . . . .	ζ_{1M}
.	.		
.	.	Rank:	
.	.	r	
.	.		
.	.		
G_g	ζ_{g1}	. . . . .	ζ_{gM}

Dimensional Analysis

Taylor series expansion of the reduced function $\phi\left(\pi_1 ... \pi_{M-r}\right)$:

$$\ln\phi\left(\pi_1 ... \pi_{M-r}\right) = \psi\left(\ln\pi_1 ... \ln\pi_{M-r}\right) \qquad ...\pi_i \geq 0$$

$$= \psi_0 + \sum_i^{M-r} \beta_i \ln\pi_i + \sum_{i,k}^{M-r} \gamma_{ik} \ln\pi_i \cdot \ln\pi_k + O(3)$$

$$\phi\left(\pi_1 ... \pi_{M-r}\right) = C \prod_i^{M-r} \pi_i ** \left(\beta_i + \sum_k \gamma_{ik} \ln\pi_k + \sum_{k,l} \delta_{ikl} \ln\pi_k \cdot \ln\pi_l + ...\right)$$

$$\cong C \prod_i^{M-r} \pi_i^{\beta_i} \prod_i^{M-r} \pi_i^{\sum_k \gamma_{ik} \ln\pi_k} ... \quad , \qquad C \doteq e^{\psi_0}$$

Energy: Scale shift invariance!

Example 1: Velocity of Molecules in an Ideal Gas

List of "relevant" variables, parameters, constants:

$w = w\,(T, p, V_m, M, R)$

	T	p	$V_m = V/N$	M	R
m		-1	3		2
s		-2			-2
kg		1		1	1
K	1				-1
kmol			-1	-1	-1

$$M = 5$$
$$G = 5$$
$$r = 5$$
$$\overline{M - r = 0}$$

$w = \sqrt{\frac{RT}{M}} \cdot \text{Const}$, Calibration Experiment: $\text{Const} = \sqrt{3}$, $w = \sqrt{\frac{3RT}{M}}$

Process Calculation (Initial value problem, ODE)

$$\rightarrow \Sigma : \quad Z(t) = \left(U(t)\,,\, V(t)\,,\, n_i(t) = \sum_{\alpha}^{A} n_i^{(\alpha)} \right)$$

Accompanying equilibrium intensive parameters at time (t):

$$S = S(U, v, n_i \ldots n_N)$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum_i^N \frac{\mu_i}{T} dn_i$$

$$\rightarrow \quad T(t)\,,\, p(t)\,,\, \mu_i(t)$$

Process equations for $\dot{U}, \dot{V}, \dot{n}_i$, Taylor-series expansion:

$$\Sigma : \quad Z(t + \Delta t) = \left(U(t + \Delta t) = U(t) + F_u(t)\Delta t + \frac{1}{2}\dot{F}_u(\Delta t)^2 + \ldots \right.$$

$$\ldots$$

$$\left. \dot{n}_i^{(\alpha)}(t + \Delta t) = \dot{n}_i^{(\alpha)}(t) + F_i^{(\alpha)}(t)\Delta t + \frac{1}{2}\dot{F}_i^{(\alpha)}(t)(\Delta t)^2 + \ldots \right)$$

Iteration procedure

Stationary Processes and States

$$\dot{U} = 0 \, , \, \dot{V} = 0$$

$$\dot{n}_i = \sum_{\alpha=1}^{A} \dot{n}_i^{(\alpha)} \, , \quad i = 1 \ldots N$$

Fundamental Inequality $(*)$

$$P_s = \sum_{i,\alpha}^{N,A} \left(\frac{\mu_i^{(\alpha)}}{T^*} - \frac{\mu_i}{T} \right) \dot{n}_i^{(\alpha)} \geq 0$$

Process Equations (Flux – Force – Relations)

Mass transfer: $\dot{n}_i^{(\alpha)} = F_i^{(\alpha)}(./.) \, , i = 1 \ldots N \, , \alpha = 1 \ldots A$

$$(./.) = \left(\frac{\mu_i^{(\alpha)}}{T^*} - \frac{\mu_i}{T} \, , i = 1 \ldots N \, , \alpha = 1 \ldots A \right)$$