Introduction to Thermodynamics of Irreversible Processes

1. Classical Theory (1)
   Discrete System, Basic Concepts

2. Classical Theory (2)
   Discrete Systems, Examples, New Fields

3. Classical Theory (3)
   Continuous Systems, Basic Concepts, Examples

4. An Outlook on
   Non-Classical Formalisms
   Internal Variables, Extended Thermodynamics
   Endoreversible Thermodynamics

Classical Thermodynamics of Irreversible Processes (1)

Introduction
History, Basic Concepts

0th Law of Thermodynamics

1st Law of Thermodynamics
Conservation Laws

2nd Law of Thermodynamics
Entropy, Clausius Inequality
Process Equations

Examples

1. Adiabatic Gas Flow
2. Ranque-Hilsch-Tube
3. Vapor Adsorption Process
4. Photosynthesis of Sugar

Literature

Linear Thermodynamics of Irreversible Processes (LTIP)

Thermodynamics of Irreversible Processes

History

1850	R. Clausius	Entropy Inequality Evolution Criterion (2nd Law)
1887	J.L. Bertrand	Entropy fluxes, production
1911	G. Jaumannn E. Lohr	Balance equation for energy, entropy etc.
1931	P. Bridgman C. Eckart L. Onsager	Thermodynamic forces and fluxes, Reciprocal-Relations, LTIP
1940	S. de Groot J. Meixner	Extension of LTIP to thermo-electromagnetic processes, relaxation phenomena
1946	I. Prigogine J.M. Wiame P. Glansdorff A. Bejan	Principle of minimum entropy production, Dissipative Structures
1955	C. Truesdell B. Coleman	Rational Thermodynamics
1960	I. Gyarmati	Variational Principle
1965	J. Meixner I. Müller D. Jon, G. Lebon	Extended Th. of Ir. Pr.
1970	J. Meixner J. Kestin	Internal Variable Formalism
1970 -	J. Sengers J. Kestin W. Wakeham	New experimental methods for Transport Coefficients
1980	B. Andresen A. de Vos J. Verhas, K.-H. Hoffmann	Endoreversible Thermodynamics
1985	W. Muschik H. Ehrentraut	Dynamic intensive parameters Contact Variables
1980 -	A.I. Zotin I. Lamprecht J.U. Keller U. von Stockar	Biothermodynamics Thermo-allometric relations

Thermodynamic System (W. Schottky, 1929)

Σ: Set of bodies surrounded by well defined boundaries exchanging with its environment (Σ*) by external operations transfer energies as

Work

Heat

Mass

......

Information
(Living Systems)

$$\Sigma : p, T, n_i, \xi_k$$

$$i = 1 \ldots N,\ k = 1 \ldots K$$

Internal processes/variables
Bridgeman, Meixner,
Kestin, Flory

$$\Sigma^* : p^*, T^*, h^{(\alpha)}, s^{(\alpha)}, \mu_i^{(\alpha)}$$

$$\alpha = 1 \ldots A$$

External & Internal Processes: Level of macroscopic description or state of system (Σ).

Simple Thermodynamic System (W. Schottky, 1929)

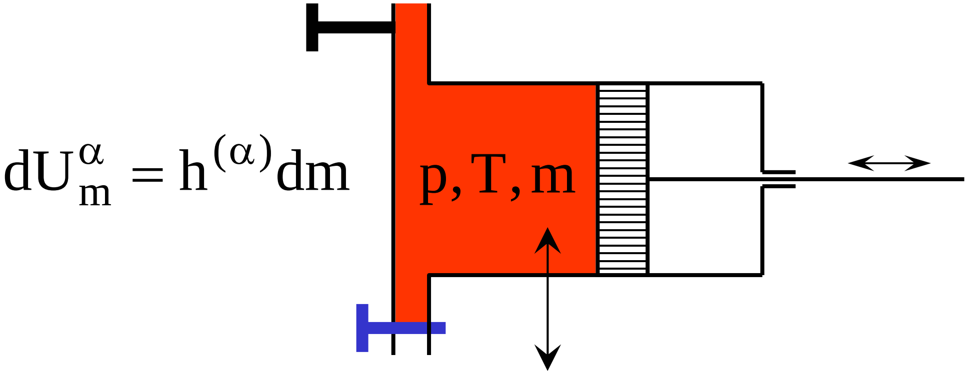
Thermodynamic System
1 Phase, 1 Component

No External forces
Surface phenomena

Radiation effects

Example: Gas in Zylinder

$$dW = -p\,dV$$



$$dQ = C...dT$$

Complex Systems: Multiphase-, multicomponent systems
Systems with fuzzy boundaries
Porous materials, Living systems (bacteria) ...

0^{th} Law of Thermodynamics

Σ: Equilibrium State
Intensive, transitive
state quantity:

1) Empirical Temperature (ϑ)

$$\vartheta = \vartheta(p, V, m_1 ... m_N)$$

Measure for warmness/coldness
Dependence on thermometer

IPTS 1990

J.C. Maxwell, L. Boltzmann
Statistical definition

2) Absolute Temperature (T)

a) Gas thermometer

$$T = \lim_{p \to 0} \frac{p\,V\left(p, \vartheta(T), m ...\right)}{\mathbb{R}}$$

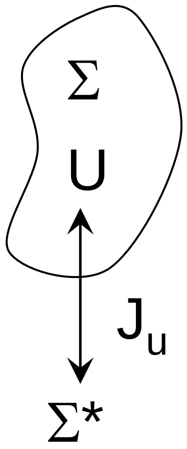
b) M. Planck (1890)
Clausius-Clapeyron-Equation

$$\frac{dp(\vartheta)}{dT(\vartheta)} = \frac{r(\vartheta)}{T(\vartheta)\left[v''(p,\vartheta) - v'(p,\vartheta)\right]}$$

$$T(\vartheta) = T\left(\vartheta^+\right) \exp \int_{\vartheta^+}^{\vartheta} \frac{v''(\vartheta) - v'(\vartheta)}{r(\vartheta)} \left(\frac{dp}{d\vartheta}\right) d\vartheta$$

1^{st} Law of Thermodynamics (1)

Σ: Any state (EQ, NEQ)
Extensive quantity of state
Internal Energy (U) (J.R. Mayer):



$$U = U(T, V, m_1 \ldots m_N)$$

$$dU = dQ - pdV + \sum_\alpha h^{(\alpha)} dm^{(\alpha)}$$

Heat Work Mass Transfer

a) Measure for ability of (Σ) to produce changes in environment (Σ*) (M. Planck)

b) Sum of all energies of molecules within (Σ)

Conservation of Energy

J.P. Joule, H. Helmholtz

$$\dot{U} = \sum_i J_{ui}$$

$$P_u = 0$$

Physics (E. Noether):
Time translation invariance of basic molecular laws.
$(t \rightarrow t - t_0)$
(Newton, Hamilton, Schrödinger, von Neumann, Liouville etc.)

1st Law of Thermodynamics (2)

Manifestations of Energy

Kinetic energy
Potential energy
Mechanical work
Heat
Chemical energy
Sound waves
Electromagnetic energy
Light

Mass (A. Einstein)

Energy Poem

W. Busch , B Ahlborn*)

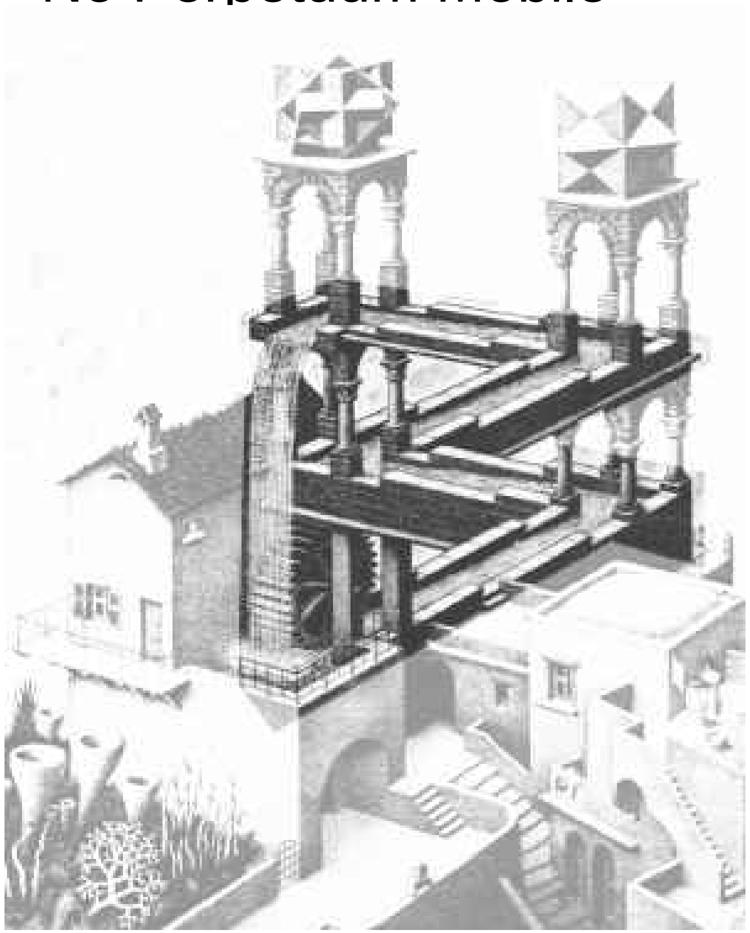
So töricht ist der Mensch…. Er stutzt	How stupid can this person get?
Schaut dämlich drein und ist verdutzt,	Looks puzzled, and is all upset
Anstatt sich erst mal solche Sachen	Instead of seeing clear and plain
In aller Ruhe klarzumachen.	The energy conversion chain.
Hier strotzt die Backe voller Saft:	Here glows the cheek, the beauty's source.
Da hängt die Hand gefüllt mit Kraft.	There rests the hand, teaming with force.
Die Kraft, infolge der Erregung,	The force, when freed by animation,
Verwandelt sich in Schwungbewegung.	Provides the quick acceleration.
Bewegung die in schnellem Blitze	This moves the hand with rapid speed.
Zur Backe eilt, wird hier zu Hitze.	The cheek receives the impact heat.
Die Hitze aber durch Entzündung	The heat excites the nerve again
Der Nerven, brennt als Schmerzempfindung	Which then is recognized as pain.
Bis in den tiefsten Seelenkern,	The pain sinks deep into the soul.
Und dies Gefühl hat keiner gern.	This is resented by us all.
Ohrfeige heißt man diese Handlung.	Slap on the face is the assertion.
Der Forscher nennt es Kraftverwandlung.	In Physics terms just Joule's conversion.

*) Zoological Physics, p. 31, Springer, 2004

1st Law of Thermodynamics (3)

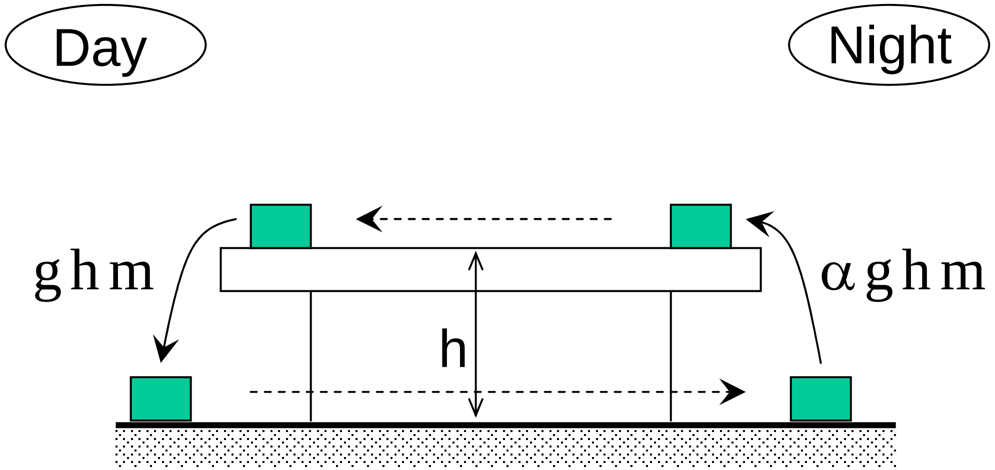
Energy Conservation

No Perpetuum Mobile



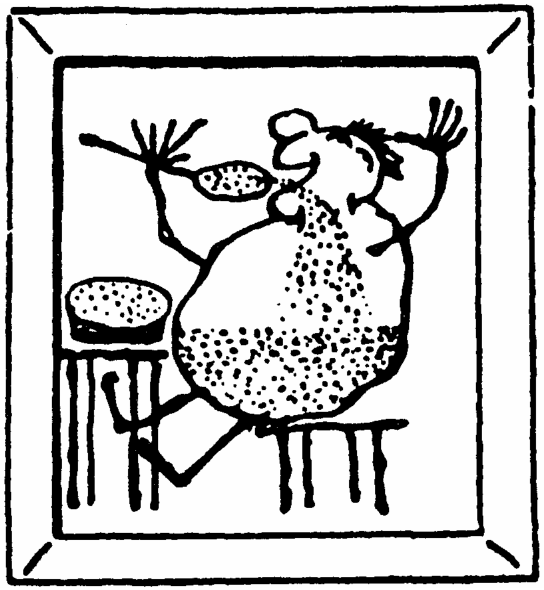
Energy Production / Annihilation

Periodic changes of (g), (T):



$$\Sigma: \quad \Delta U = (1-\alpha) g h m \gtrless 0 \ldots \alpha \gtrless 1$$

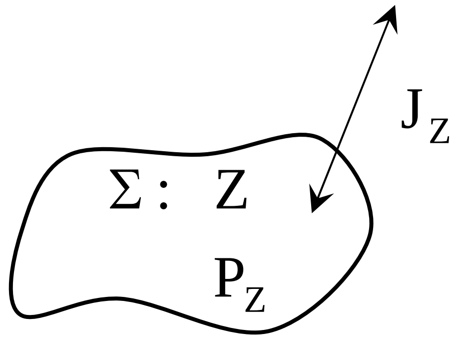
Balance & Conservation Laws



W. Busch ca. 1890

$\Sigma : Z$ ... Extensive quantity

$$\Sigma \to \lambda\Sigma \; : \; Z \to \lambda Z$$



$$\dot{Z} = J_Z + P_Z$$

Stationary State

$$\dot{Z} = 0 \,, \; J_Z = \text{const} \,, \; P_Z = \text{const}$$

Conservation Law (E. Noether)

$$P_Z = 0$$