THERMODYNAMICS – HISTORIC DEVELOPMENT

SOME APPLICATIONS AND PITTFALLS

by

Poul Scheel Larsen

Moving from curiosity driven heat-power devices to useful machines, relieving man and horse from hard labor, the need for understanding and predicting processes lead to the emergence of thermodynamics as a science.
As such it basically quantifies the system energy-content and how this changes due to energy exchange with the surroundings in the form of heat and work.
It is general, including processes in media of thermo-chemico-electro-magneto-mechanics.
It has different faces: continuum/statistical and equilibrum/non-equilibrium.
It is qualitative, telling us which processes are impossible, it is philosophical in perhaps showing the direction of the arrow of time, and it is inspiring for those measuring the information content of messages.

DTU.Mechanical Engineering – Fluid Mechanics – DCAMM 40-year anniversary – 27-11-2009

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1. Introduction

Students today and Thermodynamics ?

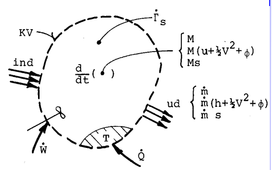
Everything is here, ready for engineering use !

Mass conservation
$dM/dt + \Sigma_{ud} m - \Sigma_{ind} m = 0$

Energy conservation (1.Law)
$d[M(u+ \frac{1}{2}V^2+gz)]/dt + \Sigma\, [(h+ \frac{1}{2}V^2+gz)m\,]_{ud} - \Sigma[(h+ \frac{1}{2}V^2+gz)m\,]_{ind} = Q+W$

Entropy balance (2.Law)
$d(Ms)/dt + \Sigma\,(sm)_{ud} - \Sigma\,(sm)_{ind} = \Sigma\, Q/T + \Gamma_S$

+ **Equations** of state, tables, diagrams …



BUT… How did we get there?

The Short Story

For years it was as to see in a glass, in a riddle…

But then to perceive and realize piecewise
to finally understand fully.

HISTORIC DIFFICULTIES

- ENERGY IN SYSTEM - ENERGY IN TRANSIT
  (Internal energy – Heat – Work)
- ABSOLUTE (thermodynamic) TEMPERATURE
- ENTROPY
- MIXING CONCEPTS (General Laws and Constitution)
  (early texts in Thermodynamics develop laws for ideal gas)

The problem of ABSTRACT CONCEPTS

What does it mean to understand?
(say energy, entropy, exergy, etc.)

Accept via what is already ’understood’
(i.e. via accepted concepts and experience)

– or you have seen it often enough that it doesn’t bother you

2. History

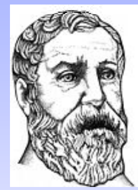
- before the heat engine

- There were 4 elements:
  - **fire**
  - **air**
  - **water**
  - **earth**

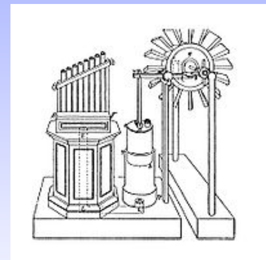
according to Greek pre-Socratic philosopher Empedocles (490–430 BC)

Timeline of heat engine technology

- 60 AD Hero of Alexandria



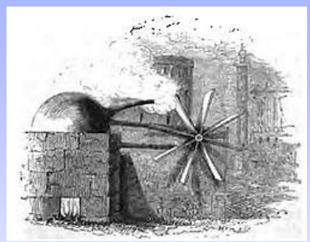
Heron's Aeolipile



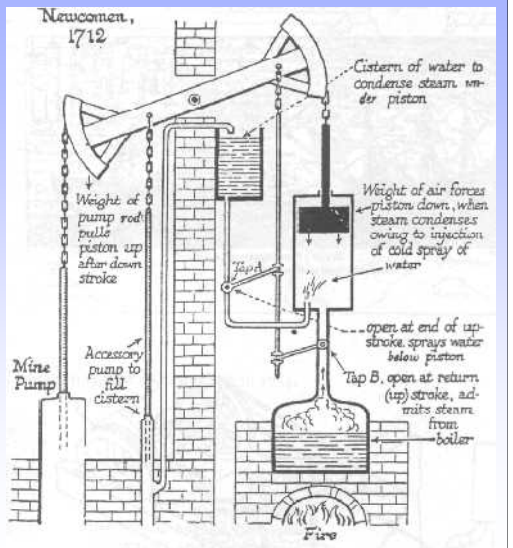
Hero's wind-powered organ

≈ 1500: Leonardo da Vinci
Steam-power cannon

- 1616 Giovanni Branca: Steam turbine



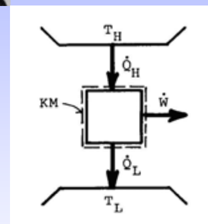
- 1698 Thomas Savery: Steam-powered water pump (water out of mines)
- 1712 Thomas Newcomen: Steam-powered water pump

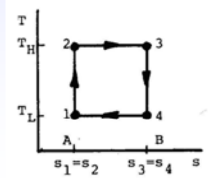


DIAGRAMMATIC VIEW OF NEWCOMEN'S ATMOSPHERIC OR FIRE ENGINE (1712)

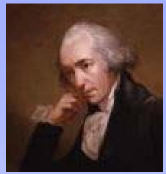
- **Sadi Carnot** (1796-1832)

- Idea that while energy might never be lost, it might become *unavailable* (1824)
- Definition of Work. Idea of cycle
- Ideal (reversible) Carnot Cycle
- Idea of Entropy, but it was Clausius that clarified it (symbol S believed to come from Sadi)

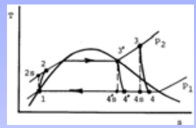




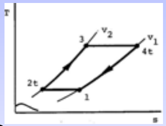
Engines

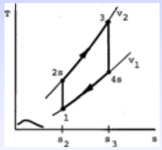


1769 James Watt: improved steam engine

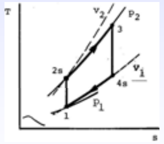


1816 Robert Stirling's hot air engine





1859 Etienne Lenoir: 2-stroke IC-engine
1877 Nikolaus Otto: 4-stroke IC-engine



1884 Charles Parson: Steam turbine
1892 Rudolf Diesel: Diesel engine

1929 Felix Wankel: the rotary Wankel IC-engine

Timeline of thermodynamic Theory

Equilibrium Thermodynamics

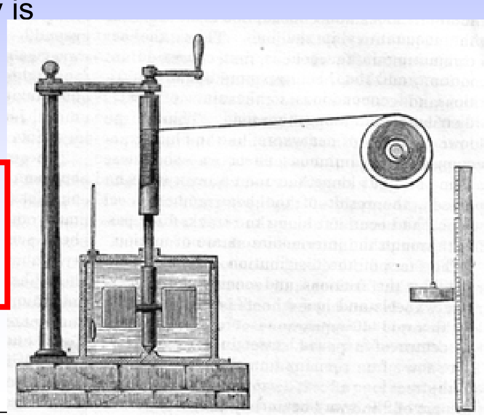
- 1676 Boyle-Mariotte law, pV = const. (at T=const.)
- 1787 Jacques Charles: gas law, p/T = const. (at V=const.) referenced by Gay-Lussac in 1802
- 1824 Sadi Carnot: the Carnot cycle
- 1849 W.Thomson (Lord Kelvin): Term *Thermodynamics* (absolute temperature + version of 2.law)
- 1850 Rudolf Clausius: Entropy and 2.Law
- 1871 James Cleark Maxwell (with Clausius): Term *Statistical Thermodynamics*
- 1876 Willard Gibbs: Gibbs free energy G (chem.thermo)

- **James Prescott Joule** (1818-1889)
- Mechanical equivalent of heat (1843)

  (i.e. measure both in the same units of energy – not HP and Cal !)
- Demonstrated by simple experiment where mechanical work energy is converted into thermal internal energy via friction

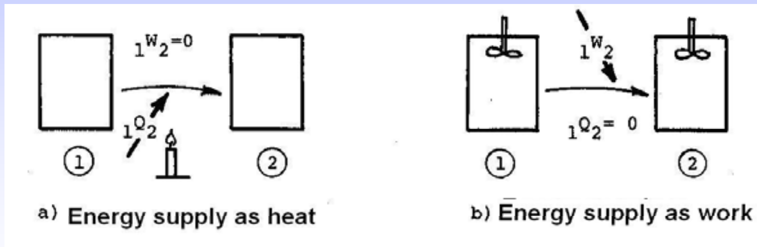
Misconception:

No heat transfer !



Energy Equivalence

- Adding the same amount of energy as either heat or work to a system at state 1, leads to the same state 2
- Examination of state 2 does not reveal how energy was supplied !



Temperature and pressure increases from 1 to 2

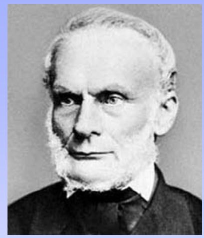
Does the gas contain Heat? – or Work?

Nonsense

- **Rudolf Clausius** (1822-1888)
- 2.Law (1850)

  What is not possible (the inequality of Clausius)

  For a **cycle** $\oint \frac{\delta Q}{T} \leq 0$



- Concept of Entropy (1865)
- For **process**: $\int_A^B (\delta Q / T)_{rev} = S_B - S_A$

  (state property, independent of path)

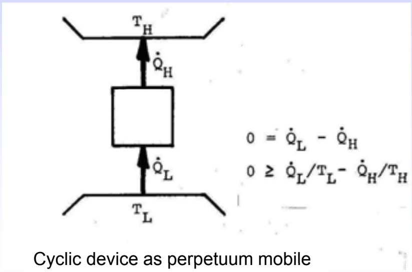
  In general: $\delta Q/T \leq dS$

  Entropy of universe tends to a max.

  Kinetic gas theory (1857)

  (include molecular rotation and vibration)

  (introduce the mean free path)



Cyclic device as perpetuum mobile

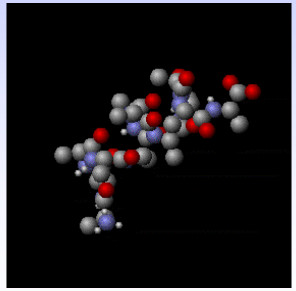
Violates 2nd Law (Clausius, 1850)

For $T_H > T_L$, unless $Q_L = Q_H < 0$

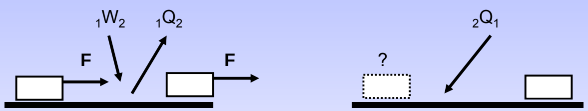
HEAT

- The concept of heat was associated with the motion of molecules in a gas
- the faster the motion, including rotation and vibration, the hotter the gas (higher temperature)
- 'kinetic temperature' – $V_{mean} \approx \sqrt{T}$

Today we say 'Internal Energy' (translation, rotation, vibration, electronic states)



- **On the 2nd Law**
- **Qualitatively**
- Experience: Some processes possible, others not



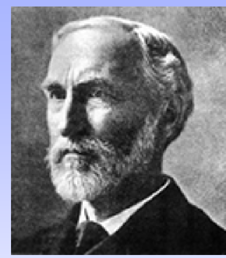
- So process is irreversible

- **Quantitatively**
- Cycle: Inequality of Clausius $\oint \frac{\delta Q}{T} \leq 0$
- Process: New state property, $(\delta Q/T)_{rev} = dS$

  In general: $\delta Q/T \leq dS$

- **Willard Gibbs** (1839-1903)

  (father of mathematical rigor in thermo)
- Gibbs free energy G (equil. thermo) (chemical potential)
- Formal relations for state properties (mixtures – the Gibbs phase rule)
- Chemical thermodynamics
- Physical chemistry



- **1848 James Prescott Joule**
- Velocity of H_2-molecules account for pressure in a gas at given temperature
- A contribution to the kinetic theory of gases

Statistical Thermodynamics

- 1871 James Cleark **Maxwell** (with Clausius):
  Term: *Statistical Thermodynamics*
- 1877 Ludwig **Boltzmann**:
  (father of Kinetic Theory of Gases and Statistical Mechanics)
- Quantify Entropy: S = k log W
  (W = number of microstates for given energy)
- The Boltzmann (transport) Equation for $nf(c_1,c_2,c_3)$

$$\frac{\partial}{\partial t}(nf) + c_j \frac{\partial}{\partial x_j}(nf) + \frac{\partial}{\partial c_j}(F_j nf) = \int_{-\infty}^{\infty}\int_{dP_c} n^2[f(c_i')f(\zeta_i') - f(c_i)f(\zeta_i)]g\, dP_c\, dV_\zeta$$

- At equilibrium: $0 = \int_{-\infty}^{\infty}\int_{dP_c} n^2[f(c_i')f(\zeta_i') - f(c_i)f(\zeta_i)]g\, dP_c\, dV_\zeta$
  yielding the Maxwell distribution of translational gas:

$$f_0 = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mC^2/2kT} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}(|c_i - \bar{c}_i|)^2\right]$$

- All state properties (U,S,H,F,G,T,p,…) expressed by molecular distribution function at equilibrium
- Moments of the Boltzmann Equation give the equations of the continuum formulation, including transport properties (k, μ)
- At global non-equilibrium, flow and transport expressed by small difference: $f \neq f_0$

- **Boltzmann's H-theorem**
  From the S-moment of the Boltzmann equation for uniform state:

$$\frac{dS}{dt} = \frac{kV}{4}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{dP_c} \ln\left[\frac{f(c_i')f(\zeta_i')}{f(c_i)f(\zeta_i)}\right] \times n^2[f(c_i')f(\zeta_i') - f(c_i)f(\zeta_i)]g\, dP_c\, dV_\zeta\, dV_c.$$

hence in approaching equilibrium

$$\frac{dS}{dt} \geq 0,$$

with $S = S_{max}$ at equilibrium (for fixed U and V)

Equilibrium = Max Entropy implies alternatives

From 1st and 2nd Law: $dS - dU/T + p\,dV \geq 0$

- $S_{U,V} = S_{max}$, $U_{S,V} = U_{min}$, $H_{S,p} = H_{min}$, $A_{T,V} = A_{min}$, $G_{T,p} = G_{min}$ where each condition depends on specific constraints
  ($H = U + pV$, $A = U - TS$, $G = H - TS$)
- Solid mechanicians often use the principle of min elastic (internal) energy at equilibrium, but this apparently assumes that both entropy and volume are kept constant as equilibrium is approached. Are they ?
- Reaction chemists use $G_{T,p} = G_{min}$, implying the law of mass action and equilibrium concentrations in reacting mixture

Generalized Thermodynamics

- Energy and energy change of system due to exchange of energy with surroundings in the form of heat and work (def. of thermo)
- Many kinds of work, not just compression/expansion of gas or liquid ($\delta W = -pdV$)
- So many kinds of media

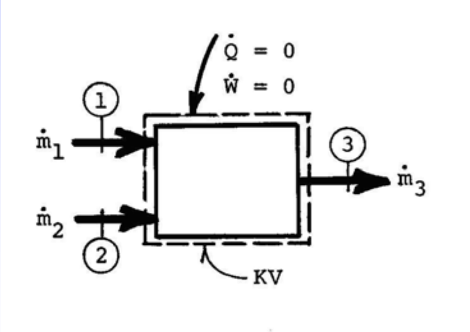
Energy exchange as generalized work

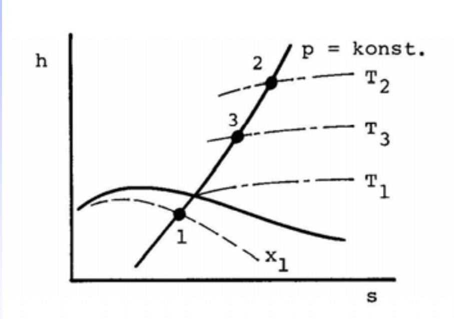
Reversible work forms $\delta W_{rev} = F_j\, dX_j$	
Mechanical	
Compression of fluid	$-p\, d\mathcal{V}$
Stretching elastic rod	$\sigma_{11}\, d(\mathcal{V}\varepsilon_{ll})$
Elastic deformation	$\sigma_{ij} d(\mathcal{V}\varepsilon_{ij})$
Stretching liquid surface	$\sigma_s\, dA$
Electric	
Polarization	$\mathbf{E}.d(\mathcal{V}\mathbf{P})$
Magnetic	
Magnetization	$\mu_0\, \mathbf{H}.d(\mathcal{V}\mathbf{M})$
Chemical	$\Sigma\mu_i\, dm_i$

3. Possible processes

Possible and Impossible Processes

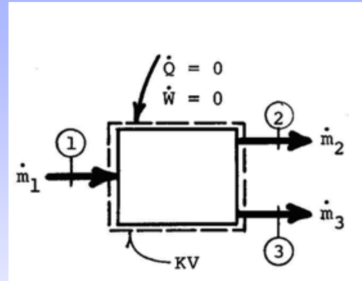
(1) Adiabatic, isobaric mixing process



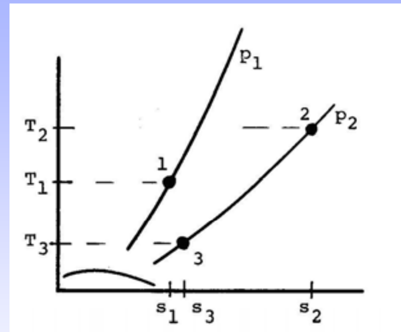


No problem. Positive entropy production (due to curvature of isobar)

- (2) Reversed adiabatic process ?

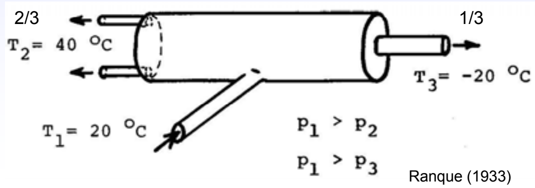


$T_2 > T_1 > T_3$



Yes, possible if $p_1 > p_2$ and p_3 in a Ranque-Hilsch device

Need not violate 2.Law !



Ranque (1933)

Anomaly: Heat transfer up temperature gradient ín stratified turbulent flow

Schultz-Grünow (1951)

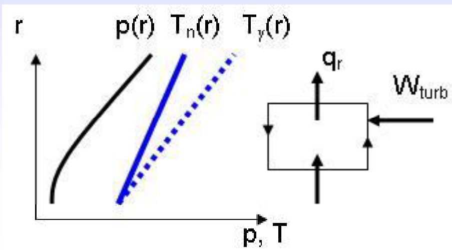
Ideal gas in stratified centrifugal force field, $r\omega^2$, at some T(r)

Large turbulent fluctuations u_θ make parcels compress/expand following some polytrop, $pv^n = \text{const.}$ Exponent n given by

$$dT/dr = (r\omega^2/c_p) \times \gamma/(1-\gamma) \times (1-n)/n$$

If $n = \gamma$: isentropic, $q_r = 0$, no heat transfer

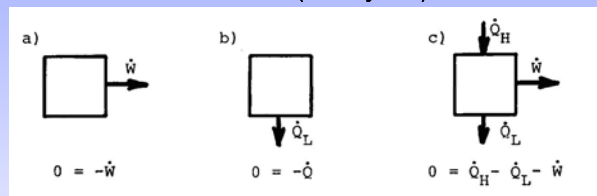
If $n < \gamma$: polytropic, $q_r > 0$, heat transfer up temp.gradient !



Inventions and Perpetuum Mobile

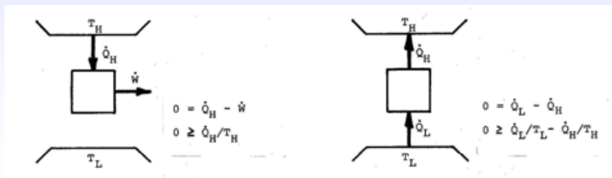
Violation of 1st Law (for cycle)

- Not common



Violation of 2nd Law

- More common



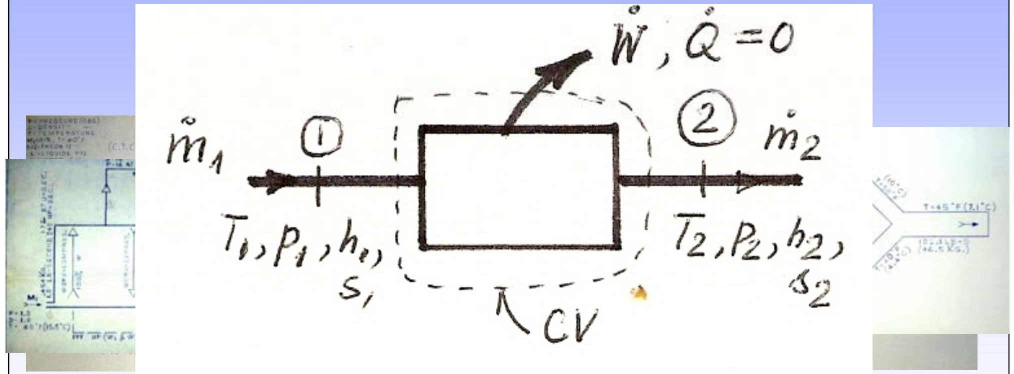
a) Kelvin-Planck statement b) Clausius statement

Invention

- Anonymous inventor will charge a 12 Volt battery at 50 Watt
- Has seen an electrolytic cell device on the web that, using a battery, produces H_2 and O_2 for a welding torch drawing up to 3000 Watt (www.h2extreme.com)
- Idea: Using his 50 Watt charge, he can get net 2950 Watt worth of useful gas to drive a gas engine

- That will solve the energy problem of his community !

INVENTION: Efficient Power Process



Air in → 15.5 C

So energy extracted !

Air out → 7.1 C

But, 2.Law violated – don't waist your time checking numbers !

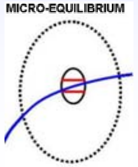
Why it is useful to know Thermodynamics

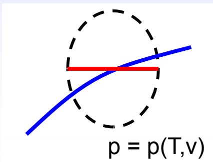
$$\sigma_{ij} = 2\mu s_{ij} + (\kappa S_{kk} - p_1)\delta_{ij} \qquad (2.3.14)$$

其中λ是第二粘性系数，而 $\kappa = \frac{2}{3}\mu + \lambda$ 叫做体积粘性系数 (bulk viscosity)。如假设体积粘性系数 $\kappa = 0$ (这个假设称为斯托克斯

- Local thermodynamic equilibrium in a compressible fluid in motion implies that bulk viscosity is zero
- If mean negative normal stress should be thermodynamic pressure, $p = -[\kappa (1/v)Dv/Dt - p_1]$, it can only depend on state properties like T,v, but not on their rate of change, where from continuity, $S_{kk} = \partial V_k/\partial x_k = (1/v)Dv/Dt$
- Polyatomic gas: micro-equilibrium for rapid process $T_t \neq T_r$, $\kappa \neq 0$

MICRO-EQUILIBRIUM





LOCAL Equilibrium for GLOBAL non-equilibrium

4. Irreversible Thermo

EQUILIBRIUM THERMODYNAMICS:

- Equilibrium States 1, 2, …
- Net change from 1 to 2 to …

IRREVERSIBLE (NON-EQUILIBRIUM) TERMODYNAMICS:

- Rate processes in space and time:

- SKALAR (Local relaxation, chemical reaction, …)
- VECTOR (Fluxes of heat, matter, charge, …)
- TENSOR (Stress, striction, … of TEMM continua)

Irreversibel Thermodynamics

(Gibbs, Onsager, Prigogine, Glansdorff , deGroot, Stengers)

From 1st and 2nd laws for continuum

entropy production = driving force × flux

$$\dot{\sigma} = \Sigma X_j J_j \geqslant 0,$$

flux = phenomenological coefficient × driving force

$$J_i = \sum_k L_{ik} X_k = L_{i1} X_1 + \ldots + L_{ii} X_i + \ldots,$$

hence

$$\dot{\sigma} = \Sigma_i \Sigma_k L_{ik} X_k X_i \geqslant 0,$$

subject to restrictions

$$L_{ii} \geqslant 0; \quad 4 L_{ii} L_{kk} - (L_{ik} + L_{ki})^2 \geqslant 0.$$

Onsager's reciprocity relations (based on micro-reversibility)

$$L_{ik} = L_{ki},$$

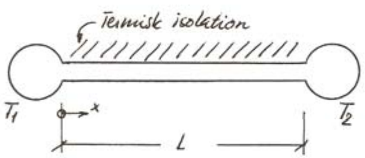
Vectorial example: Thermodiffusion

Heat and mass fluxes depend on both temp. and conc. gradients

$$\vec{q} = -k \vec{\nabla} T - \rho c_1 \mu_{11}^c T D_1'' \vec{\nabla} c_1$$

$$\vec{J}_1 = -\rho c_1 c_2 D_1' \vec{\nabla} T - \rho D_{12} \vec{\nabla} c_1$$

Binary gas mixture separated by imposed temperature gradient



$$k_T \ln \frac{T_2}{T_1} = c_1(0) - c_1(L)$$

Steady non-equilibrium: $\sigma_S = \sigma_{S,min}$

Non-Equilibrium Thermodynamics

- 1870 Willard Gibbs (1839-1903): Chemical thermodynamics
- 1929 Lars Onsager (1903-1976): Onsager reciprocal relations
- 1970 Ilya Prigogine (1917-2003): dissipative structures, minimum entropy production at steady non-equilibrium state, symmetry breaking, etc

  (*Brussels school*: Glansdorff , deGroot, Mazur, Stengers)

5. Life

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Thermodynamics and living organisms

- Yes, of course – just bio-chemistry and complexity
- Not just energy but **useful energy** matters
  (also called **exergy** or **availability**)

- What is the efficiency of an IC engine? [20-30% ?]
- What is the efficiency of a living organism, say man ?
- As a start, what is the power at rest ?
  i.e. the **basal metabolic rate (BMR)**

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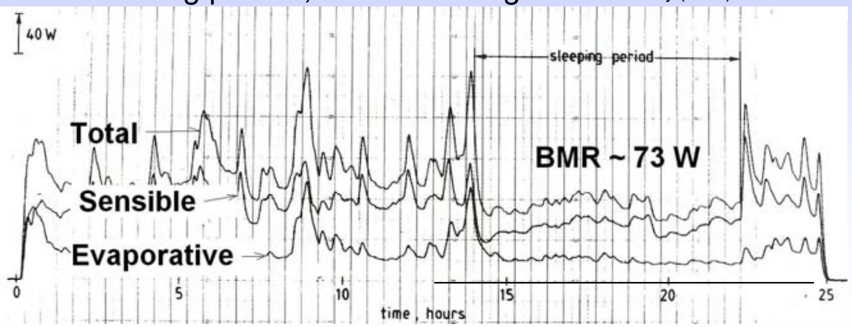
- **Human Calorimeter**
- Measure sensible and evaporate heat
- via flow, T, x

Early (1982) 5.8 m^3 chamber

- For ~ 70 kg person, BMR ~ 1 W/kg



25 h record in 24 m^3 chamber, Jacobsen et al (1985)

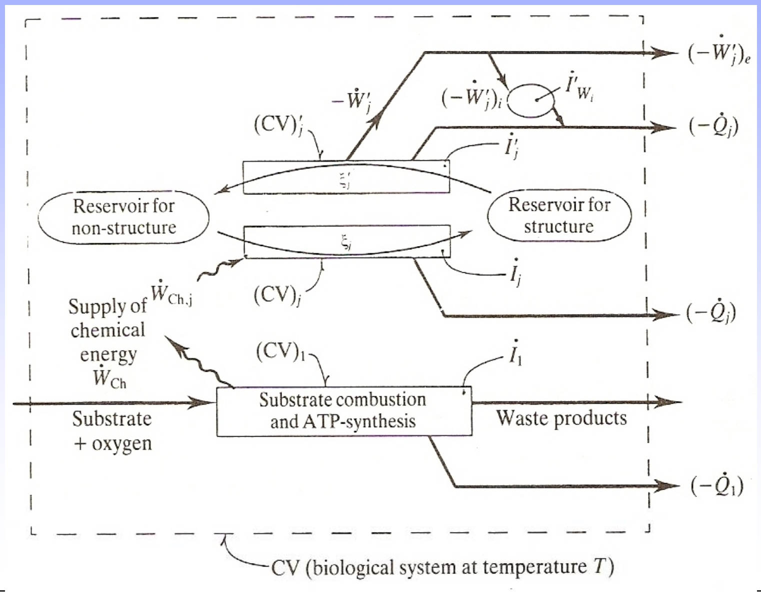
DTU.Mechanical Engineering – Fluid Mechanics – DCAMM 40-year anniversary – 27-11-2009

How to define life ?

- Structure in time and space
- Maintained by supply of useful energy (exergy)

- Other details, e.g. growth and reproduction needed to maintain populations ignored here

Model of Biological System



Estimate of exergy efficiency at rest (BMR ca. 1 W/kg)

- **70 kg person (exergy consumption: 74 W)**
- **Estimated irreversibilities at rest:**
- External work 0 W
- Internal mechanical work 2-3 W
- Ion pumps, diffusive processes 6 W
- Synthesis of large molecules 10 W
- Diverse 1-2 W
- I alt ca. 20 W
- **Exergy efficiency ca. 27%**

Man-made power-generating Systems

Require 2 heat reservoirs (except PV- and PE-systems)

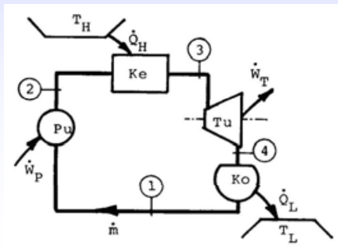
Exergy balance:

$$d(M\xi)/dt + \Sigma (\psi m)_{ud} - \Sigma (\psi m)_{ind} = \Sigma_i(1-T_0/T_i)Q_i + W - W^{UU} - I_S$$

for steady cyclic process reduces to the relation for useful work:

$$(-W^U) = \Sigma_i(1-T_0/T_i)Q_i - I_S$$

i.e. the Carnot-cycle power minus the irreversibility, $I_S = \sigma_S T_0$



Living organisms operate on chemical energy

Exergy balance for steady, no-work and isotermal processes

$$d(M\xi)/dt + \Sigma (\psi m)_{ud} - \Sigma (\psi m)_{ind} = \Sigma_i(1-T_0/T_i)Q_i + W - W^{UU} - I_S$$

reduces to the relation

$$\Delta G_r = I_S$$

so, the exergy consumption equals the irreversibility

The 1st Law gives the energy lost as heat (–Q)

$$\Delta H_r = Q$$

Conceptual process maintaining structure in time and space

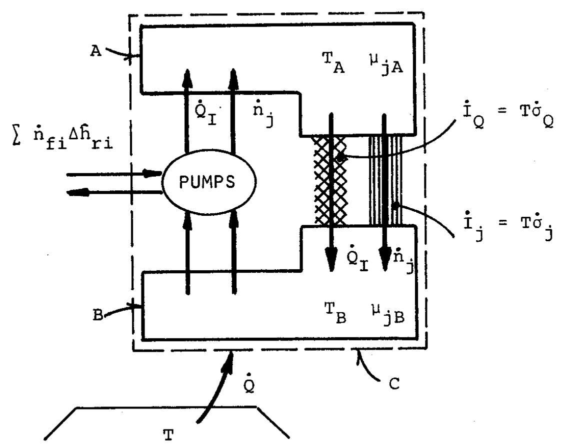
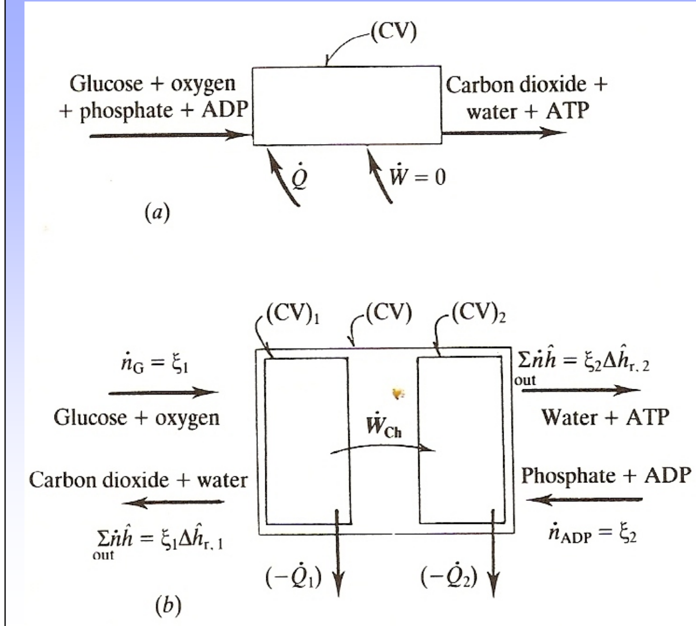


FIG. 3. Irreversible internal heat transfer ($\dot{Q}_I$) and mass transfer ($\dot{n}_j$) in composite system, maintained by ideal heat pump and ideal chemical pump, respectively.

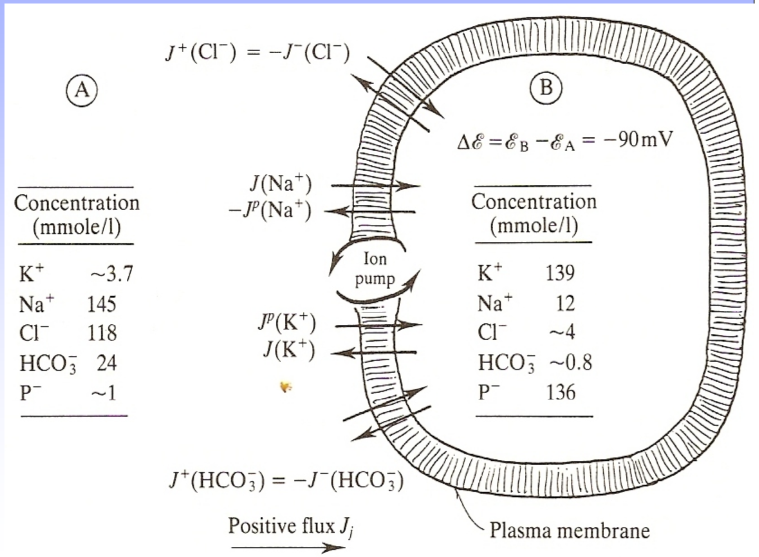


Fundamental coupled chemical reaction

Cell with ion-pumps

~10^{13} cells
~20 μm diam. in
~40 l tissue
~12,000 m^2

Na^+ flux ~ 248×10^{-10} $\frac{mol}{m^2\, s}$

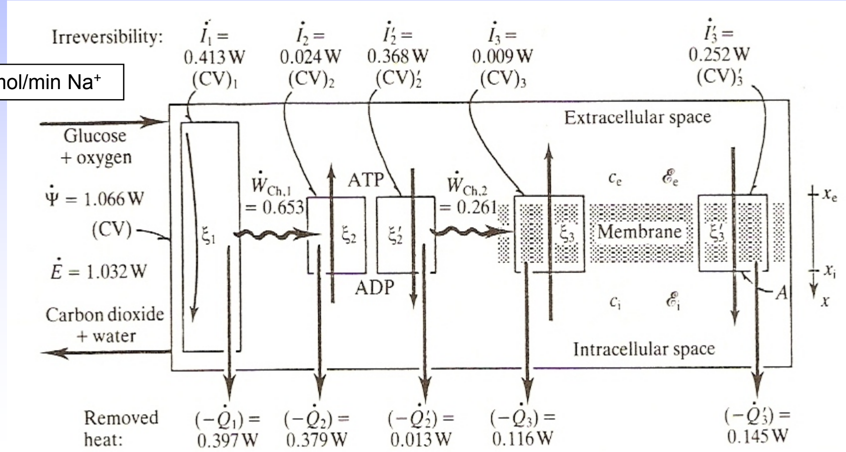


Exergy balance for ion pump

$$\varepsilon = 0.252/1.066 = 0.24$$

(efficiency for maintaining structure)

For 1 mmol/min Na^+



6. Arrow of time

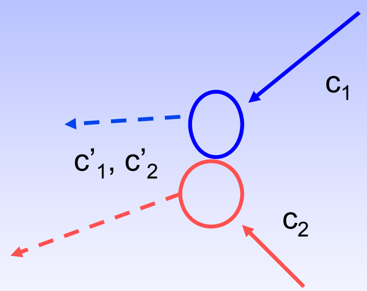
Classical dilemma of Kinetic Theory

- Consider ideal, monatomic gas (translation only)
- Use a hard-sphere elastic collision model
- Each collision is perfectly reversible
- Yet, the solution (analytical or numerical) to problem of an initial non-equilibrium distribution relaxing to the equilibrium Maxwell distribution is irreversible with a clear increase in entropy (decreasing H-function)
- How come ?
- A result of statistics: pre-collision particle-parameters are random (in Monte-Carlo simulation chosen at random), so formulation and solution procedure is not deterministic

Molecular chaos: Parameters of two colliding particles uncorrelated

- **Elastic binary collision**

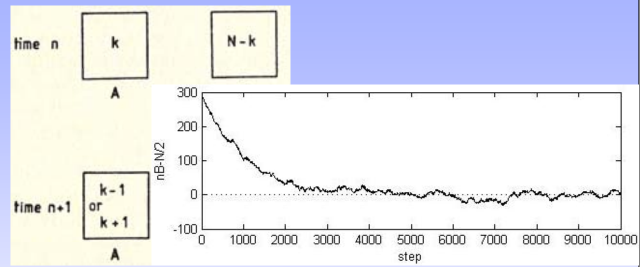
- Conservation of momentum and energy of c_1 and c_2 particles gives deterministic post-collision parameters c'_1 and c'_2
- But correlation between c_1 and c_2 unknown (non-existing i.e. Molecular chaos)



The arrow of time and increase of Entropy

Ehrenfest's urn model (a Markov process)

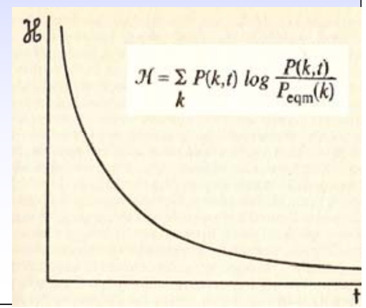
Evolution follows the Boltzmann H-function



Arrow of time is not present (apparent) in laws of nature,

-- but it's due to our decision to use present information to predict future behavior (usually by probabilistic means)

Probabilities of future events are usually determined by probabilities of past events

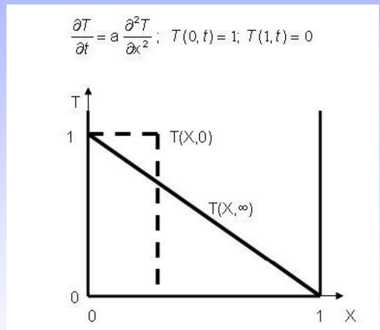


Experimentalists have no doubt of arrow of time

- Unsteady Conduction
- Solution

- Time reversal is meaningless
  - Try it ! i.e. solve

$$-\frac{\partial T}{\partial t} = a\frac{\partial^2 T}{\partial x^2};\quad T(x,0) = 1 - x;\ T(0,t) = 1; T(1,t) = 0$$



Arrow of time quote:

- **Albert Einstein**:

- "the distinction between past, present and future is an illusion – although a persisting one"
- Like quantum mechanics, he opposed introduction of irreversibility into physics

- **A wisecrack:**
- "the reason that time advances is that otherwise everything would happen at once"

Thermodynamics and Cosmology

- After 'big bang', early matter was rather uniformly distributed (high entropy?)
- As universe expanded it became very structured and organized with galaxies, solar systems etc. (low entropy?)

- How to explain?

- Perhaps gravitational fields possess entropy:
  - Low, when uniform -´High, when structured

  So, $S_{Universe} = S_{matter} + S_{gravitation}$
  - or the entropy of black holes is very large ?

PCW Davies (1983), MM Waldrop, Science, Vol. 219

7. Information

Information Entropy

- Claude Shannon (1948): Theory of communication
  Probably the most irreversible process:
  "The increase of information"
- John von Neumann (1949): call it Entropy !
- E.T. Jaynes (1957): Thermodynamic Entropy =
  "Just a special case of Information Entropy"

END