Actual candidates for second law violations

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1. Introduction

Building a perpetuum mobile is an old dream of mankind. This idea is strongly interwoven with the personal projections and imaginations we have about the world. This makes it difficult sometimes to discuss the theme reasonably. However, we believe that the all present energy crisis today with its all negative ecological and political consequences will enforce a constructive discussion of this theme for the future and we will do our contribution here.

The oldest proposal of a perpetuum mobiles stems from India and can be dated back to the 5th century A.C. [1]. A famous report about a perpetuum mobile claim was published [2] by Peter Peregrinus (about 1200 A.C.) who reported first in the medieval age about magnetism and its applications, cf. fig.1 . From now on -due to the better availability of printed media- many claims have been reported. A big compilation of such machine claims was done by Dirks in the 19th century [3]. Ord-Hume has reviewed further examples until 1977 [1]. Today the internet is the most important medium for the discussion of this theme [4].

Scientific discussion started with the development of physics in the age of illumination. Initially prominent scientist like Leibnitz, Bernoulli, Boyle and Gravesande discussed the theme positively. Either they published own proposals like Boyle and Bernoulli, cf. fig.2, either they (Leibnitz, Gravesande) gave recommendation letters for perpetuum mobile builder like Bessler [5]. However, the climate of discussion changed with time. In mechanics the Hamiltonian energy conservation destroyed in science any belief in mechanic perpetuum mobiles. In thermodynamics Clausius formulated the Second law in 1850 [6] which served successfully as a working hypothesis to predict irreversibilities. But on the other side especially this law hindered the further discussion. Today the actual mainstream thermodynamics demands that every constitutive material equation has to be compatible with the second law [7].

The typical non-working perpetuum mobiles can be classified as follows:

1) machines which are working in a potential force field.

Especially many of the older claims fall in this category, see fig. 3. The mistake in these constructions rely on the erroneous belief that the driving forces belong to a non-conservative force field which is not the case here. It is clear from the mathematics of potentials that such



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Fig.1 Peregrinus permanent magnet motor the star is an iron rotor, the magnet is the stator

Fig.2 Boyle's perpetuum mobile idea tries to exploit capillarity for energy generation

systems cannot perform working cycles permanently. After the cycle is closed the energy balance is exactly zero if any losses are neglected.

2) machines with hidden chemical or nuclear hot or cold fusion or fission processes. These sort of "perpetuum mobiles" consume a often hidden and finite stock of energy.

The really working (perpetuum mobile-like) machine is always driven by a regenerative energy input and works due to the presence of a non-conservative cyclic input. These non-conservative machines can be subdivided into:

a) systems non-conservative in time:

The working machines of this class are based on a fluctuating source of energy from the reservoir of the environment. They often have implemented an sufficiently fast feed back mechanism or





Fig.3: a non working perpetuum mobile proposal by Robert Fludd from 1618

Fig.4: the permanent ringing bell a construction of a high ohmic high voltage battery which let oscillate the small bowl between the poles periodically about 40 years

a non-linearity which allows to accumulate energy after an energy input from the fluctuating medium. The efficiency of these machines depends on the amplitude and frequency spectrum of the medium. Typical examples -if enumerated from big to small- are tide power plants, mechanical clocks reloaded



Fig.5 system with a non-conservative coupling to a conservative field

by fluctuating pressures [1] or mechanical forces, ratchet models [8], all hypotheses of so-called Maxwell demons and zero-point energy systems [9].

b) systems non-conservative in (state)-space (and as well in time):

To this class belong wind wheels and systems with non-conservative input which may be based on a non-conservative coupling or on cycles in non-conservative fields cf. fig.5 and tab.1. Other systems of this class are gradient generating battery-like material combinations using plasmas as "electrolyte". These constructions are intended to maintain a (often very significantly tiny) electrical current permanently with any significant loss of chemical energy [10]. They are nonconservative systems in the sense of the definition given in appendix 1.

All these machines become the classical perpetuum mobile of 2^{nd} kind if the driving ambient medium is thermical. This classical type of perpetuum mobile changes heat energy to mechanical energy with 100% efficiency and cools down the environment.

In this article we try to characterize these machines. We will presents in sum three systems from non-linear dynamics and classical thermodynamics as candidates for second law violations.

system	parametrisation	energy form 1	energy form 2
windmill	angle φ	"wind" field energy	mechanical energy
exotic iron moving	path x	magnetic field	mechanical energy
in magnetic field	(and time t)	energy	
parametric changing	time t	magnetic field	electric current
inductivity		energy	
parametric changing	time t	electric field energy	electric current
capacitance			

Table 1: postulated or possible realizations of non-conservative force couplings

2. Characterization of second law violating processes

In order to recognize systems correctly which may be of 2^{nd} law violating character we have to define first how these systems have to look like.

We restrict the discussion here to systems which are reproducible and come back to their initial state after a cycle. They do not change the chemonuclear consistence of matter in the environment after a cycle. It can be followed that these systems have to be described mathematically by potential function or variational functionals [11]. Both mathematical tools show exactly the necessary mathematical features in order to describe a reproducible system.

If the differentials of a potential are physically identified by work definitions then energy conservation follows after a cycle of a reproducible system. Mayer and Joule were the first who determined the energy equivalent between heat and mechanical energy. Their consideration and experiments referred initially to situations showing the most simple form of (point to point) energy conservation of equilibrium thermodynamics. In general, however, it turned out later that the situation is more complicated because normally energy conservation can be proved only after a cycle is closed due to the potential structure of thermodynamics caused by the reproducibility. If then the thermodynamic processes are independent from time the description can be reduced to a classical equilibrium thermodynamic state space potential denoted as U,H,F, or G. The entropy is generally defined over the heat definition

$$\sum_{j} dQ_{j} := \sum_{i} T_{i} dS_{i} = dU + p \, dV - \sum_{i} \mu_{i} dn_{i} + \dots$$
(1)

where is defined Q:=heat, T:=temperature, p:=pressure, V:=volume, μ_i :=chemical potential of substance, n_i := number of moles of a particle species. The points indicate here forgotten possible contributions like field energies for instance.

The entropy or the entropies S_i (especially in the case of non-equilibrium thermodynamics if the system cannot be fitted by only one temperature) are necessary functions which have to be introduced mathematically in order to be able to close the reproducible cycle in the description. Later Gibbs and Boltzmann found out that the entropy could be calculated from a probability distribution function of the particles of the considered system. Today this result is regarded to be valid in general and is not a conclusion furthermore but has changed to be a definition. For it is assumed generally that the thermodynamic and the statistic interpretation are always

equivalent despite of many different statistic forms of entropy in non-extensive-thermodynamics and despite of the further complication by time-dependent non-linear thermodynamics.

Therefore, if the particle distribution of entropy can be determined experimentally, it follows that the temperature is always defined uniquely calorimetrically over dQ := T.dS if a statistic definition of *S* like Gibbs' definition of entropy

$$S = k \iint W \ln(W) dn_i d\varepsilon$$
⁽²⁾

or another like Tsallis entropy is applied.

The Second Law according to Clausius demands that the net entropy $\oint dS < 0$ is set free after an isothermal cycle. Then *S* cannot be described completely by a thermodynamic equilibrium function of the state space because these cycles contain irreversibilities and may be time-dependent.

There exist other different (but not always equivalent) formulations for the 2nd Law. For instance the Planck-Kestin version forbids explicitly any perpetuum mobile of 2nd kind [12]. Another practically more applicable version is Kelvin's "proof" or better criterion for the impossibility of super-Carnot efficiencies for thermodynamic machines [13].

The 2nd Law is an axiom which has not been proved until today. Own trials to prove it mathematically from variation principles failed [11]. Other proofs based on thermodynamic inequalities fail as well because a thermodynamic inequality can describe only an irreversible part of a cyclic thermodynamic process and does not allow to give an generally valid answer to the question about the entropy balance after a complete cycle is performed.

In order to avoid theoretical inconsistencies with the 2^{nd} Law it was postulated by [12] that the constitutive material equations have to be built in coincidence with the 2^{nd} Law. However, we will show it later that it seems to be obvious that second law violating systems exist. Therefore, we believe that it makes more sense to characterize state space region of materials as 2^{nd} Law-compatible or not compatible with respect to a thermodynamic process or cycle. This means, the 2^{nd} Law compatibility has to be translated into material criteria as shown in [14], or in appendix 1.

3. Concrete Examples

3.1 inverted hysteresis systems

It is widely known that the hysteresis of ferroelectric or ferromagnetic materials heats up the electronic parts if they are excited periodically by an electric or magnetic field. Only recently it was discovered that there exist electronic elements where the hysteresis is reversed. Consequently, if only heat and electric work are involved in the energy balance these electronic part should deliver electric energy and cool down the environment under "isothermal" conditions according to the first law. In the following subsections we will present the known facts about these systems .

3.1.a) the FET of Yusa-Sakaki

A good example for such a possible second law violating system is the InAs-quantum dot-doted FET invented by Yusa&Sakaki [15] and reproduced by Balocco et al.[16]. Its structure is shown in fig.6. The FET was constructed for storing data by charging the gate capacitance.

The theoretical model of this FET stems from Rack et al.[17]. The PDE's of the system is:

Poisson-equation:
$$\varepsilon_0 \partial_z [\varepsilon(z) \partial_z \Phi(z)] = -\rho(z)$$
 with $\rho(z) = e[N_D^+(z) - n^{3d}(z) - n_{QD}(z)]$
current: $\partial_t n(z) = -\frac{1}{e} \partial_z j(z) - f(n_{QD}(z,t),n(z)) = 0$ (3)
recombinations: $\partial_t n_{QD}(z,t) = f(n_{QD}(z,t),n(z))$

Here are ε_0 := dielectric constant of vacuum, ε :=dielectric constant of the material, ρ :=charge density, N_D :=density of donators, n_{3d} :=charge density of electrons, n_{QD} :=charge density of electron trapped im quantum dots, n(z):=free electron density function specified in the article, *j*:=current



Fig.6: structure of an inAs-quantum dot-doted GaAs-FET

a two-dimensional electron gas (2DEG) is located in the boundary between AlGaAs and GaAs. It represents the zero potential of the system. The voltage is applied between Al layer and 2DEG.





Fig.7a the experiment of Yusa-Sakaki-cf. [16] gain hysteresis of an inAs-quantum dot- FET electron charge density of the two-dimensional electron gas (2DEG) vs. gate voltage; the orientation of the cycle area indicates a gain of electric energy



in the FET, and $f(n_{QD}, n)$ is a specific function, which characterizes the recombination process, cf. [17]. Figs.7 show the electron density_in the 2DEG (=two-dimensional electron gas) versus voltage. The diagram represents in effect the electric *Q*-*U*-energy plane, the sense of rotation of the hysteresis gives the sign of the energy exchange with the environment. Remarkable is the sign of the electric gain hysteresis of the electric cycle under isothermal conditions. Further arguments for the gain hysteresis of this electronic part can be found in [18].

It has to be mentioned that an experimental test of the electric gain by a Lissajous oscillogram is not published until today. The same holds for the cooling down effect of the electronic part after an electric cycle which would need a caloric experiment.

3.1.b) inverted magnetic hysteresis

The existence of gain hysteresis in dielectric structures leads automatically to the question whether analogous systems can exist for magnetism. In deed, an inverted hysteresis loop for magnetic layered system was discovered probably first by Gruzalski in 1977 [19].

In the meantime some more magnetic layer systems have been found by different authors [20] which reproduce this effect. A theoretical explanations exist as well [21][22]. Of course these

effects have not been investigated (at least not openly) under the aspect of energy generation. Therefore, a significant caloric experiment is still missing. A further question is about the stability of these layer systems. The lifetime of these layer systems should be high enough in order to generate significant energy in it. Before such a metastable thermodynamic cycling can be regarded as successful and real, it has to be excluded that the effect is due to chemical energy which may be set free by a change of the inner structure of the film.

Useful possible applications of inverted hysteresis may be tape wound cores used by J.L. Naudin in his reconstruction of the MEG [4], the Ecklin flux generator [4] or Searl's magnetic disk [18].

3.2. the thermodynamic mixture systems of Irinyi, Doczekal and Schaeffer

In 1928 Irinyi tested successfully the mixture benzene-water in a closed thermodynamic cycle as power increasing working medium for steam engines of locomotives [23]. It was known already that the pressure of benzene and water adds ideally in a mixture. Doczekal took over Irinyi's idea and - after intense experiments with this mixture which covered probably as well the labile states- he patented a motor using the mixture benzene-water as working medium [24]. He reconstructed an auto motor into a steam motor during the 2nd world war. The motor had a over-Carnot efficiency and worked with a temperature difference between the boiler at 160°C and the condensor at 80°C. This claim is in effect equivalent to the statement that the Second law can be violated because if this is valid the proof of Kelvin [13] disproving the existence of perpetuum mobiles can be perverted. As shown in many textbooks then a heat pump can be used to transport the heat loss of the motor cycle back from the cold pole to the hotter pole without eating up all





Fig.8a: Irinyi's steam motor M motor , C condensor, S heat exchanger, Sp liquid fluid pump, K boiler, P pump









Fig.9b: from Doczekal's patent DE155744 possible cycles with Doczekal's machine

the mechanical energy generated by the motor. So a net work cycle of both machines combined can perform mechanical work without any thermic losses.

In Doczekal's motor the condensed liquid was taken out after the adiabatic expansion. Then it was not necessary to switch on the condensor in the fluid cycle of his system. If the condensor was switched off the motor continued to work at reduced power. Therefore the machine seemed to be equivalent to a perpetuum mobile of second kind. It is not clear today whether it cooled weakly against environment in effect by non-avoidable parasitic heat losses of the working machine. The memory of this machine was revived by the journalist Hielscher (25) and recently Schaeffer (26) rebuilt Irinyi's machine which uses water-benzene as fluid performing a closed vapour





Fig.10a: the Irinyi-Schaeffer motor : the double piston construction

Fig.10b: the Irinyi-Schaeffer motor: the demonstration machine

cycle. The machine works in the range between 450°K and 350°C. Under these conditions he claims to have measured efficiencies of about 60% which is much higher than allowed by the Carnot's maximum efficiency criterion [13]. Schaeffer estimates also the efficiency theoretically, however the derivation contains errors and is too low if compared with his own claimed measurement. A corrected version of such a calculation can be found in appendix 2.

In the following we present here the results of an estimative calculation of this mixture which shows that this mixture may be used in deed in order to build a perpetuum mobile of second kind at an environment temperature of 450°C. The calculation will elucidate the scarce descriptions given by Doczekal's patent and it allows to reconstruct Doczekal's cycle.

The mixture water-benzene is the limit case of an azeotropic mixture. The gas mixes ideally meaning that the partial pressures of the single gases simply add up to the total pressure of the mixture. The polar-apolar liquid mixture demixes quite completely into two liquid phases in the region of the state space interesting here.

If the free energy of this mixture is evaluated into a Taylor expansion only terms of first order are sufficient to describe the molar free energy F of the system, i.e.

$$F(v,T,x_1) = x_1 F_1(\rho_1) + (1-x_1) F_2(\rho_2) = x_1 F_1(v/x_1) + (1-x_1) F_2(v/(1-x_1))$$
(4)

where v:=spec. volume, T:=temperature, x:=molar ratio, ρ :=molar density and indices 1stand for benzene and 2 for water. The additivity of the partial pressures follows from this ansatz according to $P = -\partial F/\partial v = p_1 + p_2 := p_{C_6H_6} + p_{H_2O}$.

Due to the Legendre transformation all other potentials have the same structure as (4). Using the ideal properties of the mixture, the phase diagram, cf. fig.11, can be constructed for not too high temperatures according to the following method [27]:

Due to the ideality of this mixture the pressure can be calculated as the exact sum of the amounts of the partial vapour pressure of benzene and water alone at temperatures below 200°C. The maximum pressure of a mixture at a certain temperature can be found as the sum of the saturated pressure of water and benzene at (or very nearby) the azeotropic point for the mixture. Then the dew lines in the p-x diagram are (almost completely) horizontal and contain the azeotropic points. Only in the very close neighbourhood of a pure substance (x=0 or x=1, omitted in fig.11) the saturated pressure of the mixture approaches the saturated pressure of each substance. The boiling line of the 2-phase area and the gas is determined by the equations



Fig.11: the P-x phase diagram of benzene-water

dotted line shows the line of the azeotropic points; liquid state above horizontal lines, two-phase area between lines of same color, gaseous state below lines of same color. Arrows denote the path of Doczekal's cycle, cf. fig.12 and text

total pressure:
$$P = p_{H_2O} + p_{C_6H_6}$$

right to the azeotropic point:
$$x_{C_6H_6} = \frac{p_{C_6H_6 \text{ sat}}}{P}$$
 (5)

left to the azeotropic point:
$$x_{H_2O} = \frac{p_{H_2O_{sat}}}{P} = 1 - x_{C_6H_6}$$

where the index *sat* denotes the saturated state of the mixed vapour.

In order to calculate the thermodynamic cycles we use the oldest theory of binary mixtures - i.e. Mollier's theory developed for wet air[28]. This theory works exactly under the conditions listed above (ideal mixing of the gas, complete demixing of the liquid, the gas is regarded to be ideal). We modify the theory here for the system water-benzene. The idea is:

In the phase diagram on the left side of the azeotropic point water corresponds to the liquid, benzene to the air, on the right side the roles are interchanged.

In order to write the program the following equations are needed to describe the mixture; The vapour pressure of the "steam" has to be determined at the relevant temperature T with a an adequate vapour pressure equation [29]. Then, due to the ideal gas law the ratio X_{sat} of saturated "steam" can be calculated either in mass units as mass of "steam" (in kg) /per mass "air" (in kg) [28] either as molar ratio x of "steam" in the mixed gas (M denotes molecular masses)

in mass units:
$$X_{sat} = M_{steam} p_{sat} / (M_{air}(P - p_{sat}))$$

in molar units: $x_{sat} = X_{sat} M_{air} / (M_{steam} + M_{air} X_{sat})$ (6)

This allows to calculate the saturated enthalpy of the "steam-air" mixture

in mass units:
$$H_{sat} = Cp_{air}\Delta T + X_{sat} (Cp_{steam}\Delta T + r);$$

in molar units: $h_{sat} = Cp_{air}M_{air}\Delta T (1 - x_{sat}) + x_{sat}M_{steam}(Cp_{steam}\Delta T + r)$ (7)

Here ΔT is the difference from a arbitrary chosen reference temperature T_0 for which is taken 0° C for water. At this temperature the enthalpy of evaporation *r* and the specific heat *Cp* are determined as well. This allows to calculate the total molar enthalpy *h* of the liquid-gas mixture

$$h = Cp_{air}M_{air}\Delta T (1 - x_0) + x_g x_{sat} M_{steam} (Cp_{steam}\Delta T + r) + (1 - x_g) M_{steam} Cp_{liquid}\Delta T$$
(8)

where x_0 is the content of water in liquid-gas mixture and x_g is the molar content of the gas phase. The use of x_g becomes necessary if the expansion or compression crosses the dew line at $x_0=x_{sat}$ and the process moves into the 2-phase-area. Then, the initially given molar content of "water" x_0 becomes higher than x_{sat} and it is necessary to determine the molar content x_g of gas-liquid mixture. The molar ratio of "air" in the mixture is $(1-x_0) = x_g \cdot (1-x_{sat})$. Therefrom follows

$$x_g = (1 - x_0) / (1 - x_{sat})$$
(9)

For the calculation of the cycle the isentrope is necessary which is difficult to determine using

the old methods of Mollier theory. We obtain the isentrope by the following method: We remember the equation for enthalpy dH = VdP + TdS. If we have an isentrope it holds dS=0. Therefore we obtain an equation for the isentrope, namely

$$dh = VdP$$
 or $h_{n+1} = h_n + V(P_{n+1} - P_n)$ (10)

This additional equation allows to determine iteratively the isentrope if an initial point is given. The scheme to determine the isentrope is the following, cf. appendix 3

- calculate the first point from the initial values set *T*, *x*, *P* and calculate $p_{sap} x_{sap} h_{sap} h, x_{g}$
- **for** the next point of the isentrope
 - \bullet set *P*
 - solve $h_{n+1}(T_{n+1}) = h_n(T_n) + V(P_{n+1} P_n)$
 - for T_{n+1} by iteration using the equation of state
 - determine the final values p_{sav} , x_{sav} , h_{sat} for the point end of the loop

The results of the calculation are shown in fig.12 to fig.14. If the results are compared with the patent of Doczekal, cf. fig. 9, a good explanation for these cycles can be found:

We set the system initially to the upper temperature given from the boiler. It contains a saturated water-benzene vapour mixture of N particles of the specific volume v_g whose total volume is $V_0 = v_g * N$. Then, the piston is expanded isentropically until the temperature is cooled down adiabatically to a range between 450 °C and 350 °C. By this procedure only a ratio x_g of all N particles in the piston volume remains gaseous and a ratio $(1-x_g)$ of (only) water condenses. The benzene remains completely in the superheated state, cf. fig. 11. Then, the liquid water is separated from the gas and is recompressed to the initial starting pressure by a pump, whose energy is neglected here in the following because this amount of energy is negligible compared with the gas compression. The remaining gas is recompressed adiabatically until it reaches the initial temperature of 176.85°C. Remarkable for this procedure is that the compression adiabate



Fig.12a: Doczekal p-v-cycle calculated

the cycle consists of: 1) an isentropic adiabatic expansion (red full line), 2) a separation of the phases, 3) an adiabatic isentropic compression to the switching point (blue full line) 4) an isotherm compression to the initial pressure (full green line) 5) an evaporation of the condensed fluid(on the full green line), Note the net gain work arean in the left upper corner of the diagram!



Fig.12b: Doczekal T-v-cycle calculated

the cycle consists of: 1) an isentropic adiabatic expansion (red full line), 2) a separation of the phases, 3) an adiabatic isentropic compression to the switching point (blue full line) 4) an isotherm compression to the initial pressure (full green line) 5) an evaporation of the condensed fluid (on the full green line)

lies only very slight above the expansion adiabate. This is different to other mixtures like waterair where the difference between the compression and the expansion adiabate is greater leading to higher losses. As shown in fig.12a+b the temperature of the recompressed mixture rises faster and, if 450°K are reached, the volume of the compression adiabate is bigger and the pressure *P* is lower if compared with the expansion adiabate. In order to close the cycle the volume is compressed now back to the starting pressure P_0 on the isotherm path. Here the gaseous volume is smaller than at the starting point, namely $V_4 = v_g * N * x_g$. If the separation between liquid and gas is removed the liquid can evaporate again taking heat from the environment of 450°C, the piston removes to the initial position and the cycle can start again.

The remarkable point of this crossed cycle is that there exist regions of performance where the balance of work can be negative after the cycle, meaning that work is given off under quasiisothermal conditions. Due to energy conservation then net heat must be taken from the environment at 450°C. This means: These cycle are very pure second law violating cycles. The source code of the program contains some approximations:

 The liquid volume which falls out during the expansion is neglected. We convinced us that if we assume an overestimated constant liquid volume - the result is not changed significantly.
 The gaseous phase is assumed to be ideal.









3) The heat capacity of each component was taken as an extrapolation number in order to be near to the real enthalpy.

The last two inaccuracities can be avoided using the data for h from an exact equations of state. If our results can be confirmed by a more accurate real state calculation and an experiment the following main questions should be answered in the future: Can this cycle be made more efficient and is it possible that it can be proceeded at environment temperature ?

We suggest here some first ideas to overcome this problem:

1) To solve the temperature problem it may be possible

a) either to seek for azeotropic mixtures which work similarly at environment temperatures.

b) either to implement jet turbine like compressors in order to preheat up adiabatically the heat delivering gaseous fluid of environment to the working temperature.

2) Because an isotherm is difficult to realize technologically the isotherm of the cycle can be replaced by a piecewise path approaching the isotherm. This can be done technologically by leading the fluid through many short adiabatic turbine stages (or pistons) interchanging with heat exchangers which perform an isobar change of state.

3) In order to enhance the relative small gain of the Doczekal cycle it should be prolonged to higher pressures by adiabates. This needs a carburetor in the motor, cf. fig.15 below.



Fig.15: proposal for a Doczekal p-v-cycle enhanced for higher gain

red lines: adiabatic expansions, blue lines: adiabatic compressions, green lines: isotherms; this cycle needs an injection of liquid benzene before the expansion. It was perhaps realized in Doczekals motor

Appendix 1: Generalization of the conservative property in the sense of group theory

First we give some examples in order to be able to make the abstraction later and to formulate the appropriate definition useful to be a tool in order to test for gain cycles.

Example 1: energy differences in a force field between points on different paths, cf. Tab.1 From a force field in space we take out 4 points. We assume in the field to be test charges on which the forces act at these points. We calculate the force differences between the charges at these different points. According to tab. 2 this "energy" difference between P1 \rightarrow P3 is 3. If one returns directly P3 \rightarrow P1 the difference -3 and the sum of both pathes is 0. But, if one returns over P2, i.e. P3 \rightarrow P2 \rightarrow P1 then the "energy" differences are summed up to -4+2=-2 ! This means: the sum of this cycle is for this way

P1→P3→P2→P1 = 1.

Because the result is different from zero after a cycle this field is called non-conservative. In physics, chemistry and material science there exist many systems to be tested for energy conservation . For one-dimensional potentials I remember to the electrochemical row of potentials, to the transition matrix for the spectral states in quantum mechanics, to the Hess heat theorem in thermodynamics and the table of different thermovoltages of the materials showing the Seebeck-effect. If the potential differences are represented in a matrix for these effects as

from	point1	point2	point3	point4
 to				
point1	0	2	-3	-5
point2	-2	0	-4	-11
point3	3	4	0	-8
point4	5	11	8	0

Table	2:	Energy	differences	between	the	points	in	а	field
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done above, a zero has to be the result after a closed cycle. Otherwise energy conservation may be violated. The idea can be generalizeded principally as well for the other conserved quantities like momentum and angular momentum.

example 2: cycles with exchange rates of currencies

Something analogous can be done with exchange rates of currencies. If there exist a table of exchange rates on different stock markets one can try to run money on different paths over the different stock markets. If the exchange rates from table 2 are valid a gain is not possible (overlook the errors in the last digits) on any path. Because any "arbitrage deals" are impossible in any cycle we call the matrix "conservative".

Abstraction of the problem:

From these examples the following question arises:

What are the properties of conservative matrices whose closed cycles are proceeded always without gain or loss. For cycles using the addition as operation the "energy" difference or the gain is zero after a cycle, for a cycle using the multiplication as operation the overall factor at the end is 1 after the cycle is closed. If this is not the case it is possible to run the money in a closed cycle over the different stock markets and to win money (without any useful work). Under this conditions the markets are not in equilibrium, the matrix is non-conservative.

Table 2: exchange rates of different stock markets on 12.6.03

place	London	Frankfurt	New York	Tokyo
	(Pfund)	(Euro)	(Dollar)	(Yen)
currency				
Pfund	1	0.70	0.5932202	0.0503597122
Euro	1.428571	1	0.8474576	0.0071942446
Dollar	1.68571378	1.18	1	0.0084892086
Yen	198.571369	139	117.7966	1

Is it possible to find a test operation to check whether the matrix is conservative ? To answer this question we regard the elements a_{1i} und a_{3i} from the first and third line of table 2. We multiply the element a_{31} with every element of line 1. If all elements of the new calculated row 1 coincide with line 3, then these rows of the matrix of the exchange of currencies are conservative, i.e. if

$$a_{3i} = a_{1i} \cdot a_{31}$$

In this case we say the lines are "multiplicatively" dependent. The analogue can be done with table 1. Row n is compared with row m. Due to the additivity of work it holds for the worked performed on a path over three points

$$\mathbf{a}_{\mathrm{ni}} = \mathbf{a}_{\mathrm{mi}} + \mathbf{a}_{\mathrm{nm}}$$

if the field is conservative.

If a_{ni} is correctly transformed according to this operation then the lines are "additively dependent". If the operation can be done with all lines no gain or loss can be obtained in a closed cycle. Under this conditions the set in matrix is conservative and determined by one line. If the lines are multiplicatively dependent they can be representented as well additively if one writes.

$$\log a_{ni} = \log a_{mi} + \log a_{nm}$$

Thus conservativeness can be generalized in the following way:

We have a matrix M containing a set of elements a_{ik} . Then we can write down generally the generalized definition of the conservative property of groups as follows: A matrix is called conservative, if all elements i of a row of a matrix can be transformed into another row according to the transformation

 $a_{ni} = a_{mi} \circ a_{nm}$

Appendix 2:

In [26] Schaeffer tries to estimate the efficiency of the Rankine cycle with the mixture waterbenzene. The basic idea of the proof is to determine the enthalpies of evaporation for the mixture benzene water from the vapour pressure curve. To do this he uses the Clausius-Clapeyron equation for simple substances. This is one mistake in his proof. The correct equation to be used is the vapour pressure curve for binary mixtures, cf. [28] eq. (330).

This equation can be rewritten

$$h := x_1''(h_1' - h_1'') + (1 - x_1'')(h_2' - h_2'')$$

$$= T \left(\frac{\partial p}{\partial T} \left[x_1''(v_1' - v_1'') + (1 - x_1'')(v_2' - v_2'') \right] + \frac{x_1'' - x_1'}{1 - x_1'} \left(\frac{\partial \mu_1'}{\partial x_1} \right)_{T, p} \frac{\partial x_1'}{\partial T} \right)$$

$$\approx T \frac{\partial p}{\partial T} \left[x_1''(v_1' - v_1'') + (1 - x_1'')(v_2' - v_2'') \right]$$
(12)

Due to the insolubility of benzene in water (in the model is always $x_1 = 0$) the $\partial \mu_1 / \partial x_1$ term on the right side the second line of (12) can be taken for zero. This means: the sought values of the enthalpy of evaporation (the left side of equ. (12) add up according to the lever rule and can be calculated more simple by using thermodynamic tables.

Schaeffer's second error lies in the belief that the isentrope lays on the vapour pressure curve for saturated steam. According to our calculations the isentrope is not identical with this curve but lies below the saturated vapour pressure curve at the same temperature. Therefore Schaeffer's Rankine cycle has to be determined newly. Probably it is a quasi-Rankine cycle shown in fig.16a) +b). The cycle works as follows:

point $1 \rightarrow 2$: isobar + isotherm; point $2 \rightarrow 3$: isentrope; point $3 \rightarrow 4$: isobar ; point $4 \rightarrow 5$ isobar + isotherm; point $5 \rightarrow 1$: (for fluid) first isentropic then isobar ; The states of the different points of the cycle can be calculated from the program to be

point 1:
$$T_1 = 176.85^{\circ}$$
C, liquid state, $p_1 = 19.0912$ bar, $x = 0.5088$ point 2: $T_2 = 176.85^{\circ}$ C, saturated vapour, $p_2 = 19.0912$ bar, $x = x_{sat} = 0.5088$ point 3: $T_3 = 86.2093^{\circ}$ C, $p_3 = 1.3333^{\circ}$ bar, $x_G = 0.9394$, $x = x_{sat} = 0.5416$ point 4: $T_4 = 76.85^{\circ}$ C, saturated vapour, $p_4 = 1.3333^{\circ}$ bar, $x_{sat} = 0.68774$ point 5: $T_5 = 76.85^{\circ}$ C, saturated liquid state, $p_5 = 1.3333^{\circ}$ bar, $x = 0.5088$ point 6: $T_6 \approx 76.85^{\circ}$ C, liquid state, $p_6 = 19.0912^{\circ}$ bar, $x = 0.5088$



Fig.16a: the Irinyi-Schaeffer Rankine cycle qualitative p-v diagram of the cycle



Using these values, table 3 and the h_mol_ex values of the program, cf. appendix 3 we calculate the following enthalpy differences between the points

point 1 \rightarrow 2:	isobar evaporation:	$\Delta h_{12} = 30.664 \text{ kJ/mol}$ (data from table 3)
	using $\Delta h_{12} = h_2 \cdot h_1 =$	$x.(H_{C_6H_6} - H_{C_6H_6}) M_{C_6H_6} + (1-x).(H_{H_2O} - H_{H_2O}) M_{H_2O}$

point 2 \rightarrow 3: adiabatic expansion: $\Delta h_{23} = -8.6 \text{ kJ/mol}$ (data read off from program) using $\Delta h_{23} = h_3 \cdot h_2$

point 3 \rightarrow 5 isotherm compression with condensation: $\Delta h_{35} = -34.0803 \text{ kJ/mol}$ (from table 3) with $\Delta h_{35} = h_5 \cdot h_3 = h_5 \cdot (h_1 + \Delta h_{12} + \Delta h_{23})$ and $h_{1/5} = x H_{C_6H_6} M_{C_6H_6} + (1-x) H_{H_2O} M_{H_2O}$

- point 6 \rightarrow 5 adiabatic compression: Δh_{56} is not necessary to be calculated here
- point 6 \rightarrow 1: isobar heating: $\underline{Ah_{61} \approx 11.7 \text{ kJ/mol}}$ (estimative data for C_p from [30]) using $\Delta h_{61} = C_p \Delta T$ with $C_p = x C_p^{mol} (C_6 H_6) + (1-x) C_p^{mol} (H_2 O)$

Due to dh = v dp + T dS and dp = 0 we can identify $Q_{12} = \Delta h_{12} > 0$, $Q_{35} = \Delta h_{35} < 0$ and $Q_{61} = \Delta h_{61} > 0$ as exchanged heats. Therefrom we calculate the efficiency to be

$$\eta = \frac{Q_{12} + Q_{61} + Q_{35}}{Q_{12} + Q_{61}} \approx 19.5\% < \eta_C := \frac{T_{450} - T_{350}}{T_{450}} \approx 22.2\%$$
(13)

According to the estimative calculation here the Rankine cycle of the mixture yields efficien-cies near to Carnot's maximum and comes near to Irinyi's claimed measurement.

		-								
units: en	ergies H	in kJ/kg	5	volum	e V in n	n ³ /kg	entrop	ies S in kJ	/(kg.g	grad)
benzene:	Mwt	78.108	g/mol							
T(K) p/(bas	r)	V′.10 ³		V″.10	3	H'	Η″	S'		S´´
450°K 9.746)	1.43		42.47		47.5	367.9	3.0095		3.7215
350°K 0.917	,	1.209		397.1		-160	239.7	2.4937		3.6357
water:	Mwt	18.016	g/mol							
T(K) p/(bar	r) V´.1($)^{3}$	V″.10 ⁸	3	H'	Η″		S'	S″	
450°K 9.32	1.123	3	210.88	3	747.7	2773	8.9	2.105	6.61	299
350°K 0.416	35 1.02	72	3851.3		321.69	2638	3.4	1.03766	7.65	75

Table 3: the thermodynamic properties of the benzene and water [30]:

Appendix 3:

	water	benzene	
Molwt	18.015	78.108	molecular weight
Tc/(K)	647.2	562.2	critical temperature
Pc/(Pa)	221.2*10^5	48.9*10^5	critical pressure
$CpD/(kJ*kg^{-1}*K^{-1})$	2.2	1.2	specific heat of "steam"
$CpL/(kJ*kg^{-1}*K^{-1})$	2.2	1.2	specific heat of "air"
$CpW/(kJ*kg^{-1}*K^{-1})$	4.3	2.1	specific heatof"liquid"
r	2501.6	442	evaporation enthalpy

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