JAMES WATT'S EXPERIMENTS

www.history.rochester.edu/steam/thurston/1878/Chapter3.html
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In 1878 Thurston wrote about Watt's experiments with expanding saturated steam:

"The variation of steam pressure is approximately inversely proportional to the variation of its volume. Thus, at half-stroke, the pressure becomes one-half that at which the steam was supplied to the cylinder. At the end of the stroke it has fallen to one-fourth the initial pressure. The pressure is always nearly equal to the product of the initial pressure and volume divided by the volume at the given instant. In symbols: \( P = \frac{nrT}{V} \)

\[ nrT = V1.P1, \quad \text{thus: } P2 = V1.P1/V2 \]

and \( P1.V1 = P2.V2 \),
which is the isotherm relationship!

"It is seen that the work done per unit of volume of steam as taken from the boiler is much greater than when working without expansion. The product of the mean pressure by the volume of the cylinder is less, but the quotient obtained by dividing this quantity by the volume or weight of steam taken from the boiler, is much greater with than without expansion. For the case assumed and illustrated, the work done during expansion \((W)\) is one and two-fifths \((1.4)\) times that done previous to cutting off the steam \((P1.V1)\), and the work done per pound of steam is 2.4 times that done without expansion."

In the calculations below, \( x \) is the so called quality of wet steam, meaning the part of which is gaseous, so \((1-x)\) is the water part. Hence, \( x \) varies between 1 and 0 (times 100 is in %)

\[
\begin{align*}
\text{Start expansion conditions:} & \\
P1 & := 100 \text{ kN/m}^2 \ (\text{kPa} = 1 \text{ bar}) \\
\text{Enthalpy } & i1 := 2675 \text{ kJ/kg} \\
\text{Volumity: } & v1 := 1.7 \text{ m}^3/\text{kg} \\

\text{End expansion conditions:} & \\
P2 & := 25 \text{ kN/m}^2 \ (\text{kPa} = 0.25 \text{ bar}) \\
\text{Gaseous part enthalpy } & i_{2g} := 2618 \text{ kJ/kg} \\
\text{Gaseous part volumity: } & v_{2g} := 6.2 \text{ m}^3/\text{kg} \\
\text{Liquid part enthalpy: } & i_{2liq} := 272 \text{ kJ/kg} \\
\text{Liquid part volumity: } & v_{2liq} := 0.001 \text{ m}^3/\text{kg}
\end{align*}
\]
Watt's charge fluid wasn't precisely a dry saturated steam, not only because of some condensation during charge from the boiler, but most of all because he needed to fill water in the rim of the piston seal, in order to avoid excessive leakage. The technology of his time couldn't make a good circular fitting between piston and cylinder.

In the following we will add water to the charge and calculate how much it was to comply with the volume ratio that Watt used.

Start condition (dry saturated steam):
\[
P_1 := 1 \cdot 10^5 \quad v_{1s} := 1.6938 \quad v_{1w} := 1.0431 \cdot 10^{-3}
\]
\[
h_{1s} := 2675.25 \quad h_{1w} := 417.55 \quad \text{(enthalpies from table values)}
\]
End condition (at Watt's condenser pressure)
\[
P_2 := 0.25 \cdot 10^5 \quad v_{2s} := 6.20 \quad v_{2w} := 1.0199 \cdot 10^{-3} \quad h_{2s} := 2617.69
\]
\[
h_{2w} := 272.033 \quad \text{(enthalpies from table values)}
\]

**Watt used a quarter cutoff, thus Volume Ratio:** \( V_r := 4.0 \)

Mind that he empirically found this ratio to give the best result, not by coincidence!

Given water content at charge \( V\% \)

\[
x_1 = \frac{v_{1w} \cdot (100 - V\%) }{v_{1w} \cdot (100 - V\%) + V\% \cdot v_{1s}}
\]

energy balance
\[
W = h_{1s} \cdot x_1 - h_{2s} \cdot x_2 + h_{1w} \cdot (1 - x_1) - h_{2w} \cdot (1 - x_2)
\]

polytropic relationship
\[
P_1 \cdot (v_{1s} \cdot x_1)^n = P_2 \cdot (v_{2s} \cdot x_2)^n
\]

adiabatic relationship
\[
P_1 \cdot v_1^\kappa = P_2 \cdot v_2^\kappa
\]

\[
\begin{align*}
\begin{bmatrix} n & \kappa \\ v_1 & v_2 \\ V\% & W \\ x_1 & x_2 \\
\end{bmatrix} &= \text{MinErr} \\
\begin{bmatrix} n & \kappa \\ v_1 & v_2 \\ V\% & W \\ x_1 & x_2 \\
\end{bmatrix} &= \begin{bmatrix} 1.00 & 1.00 \\ 0.45 & 1.82 \\ 0.17 & 62.92 \\ 0.27 & 0.29 \\
\end{bmatrix}
\end{align*}
\]

\( n = 0.999071918855 \quad \kappa = 1.00000000000 \)

The polytropic exponent \( n \) is due to heat exchange and is close to 1, meaning the isotherm case by absorption of external heat (as much as work is done - not possible in Watt's machine).

The adiabatic exponent \( \kappa \) is a property of the fluid: \( C_p/C_v \), and it is practically equal to \( n=1 \), meaning that the latter is not due to any external(!) heat exchange, but is a physical property of the fluid. There is energy balance, so the increased steam quality, \( x_2 > x_1 \), can only be due to increased mass of the dry steam part, by the evaporation of some water in the rim of the piston, while doing work. Naturally, because that water was added saturated in this calculation.
The entropy difference for the steam part:

$$S_{2s} \cdot x_2 - S_{1s} \cdot x_1 = 0.32$$

is as much positive, as that of the water part is negative:

$$S_{2w} \cdot (1 - x_2) - S_{1w} \cdot (1 - x_1) = -0.32$$

thus a net zero change. This means that the process goes adiabatically, no heat exchange with the surroundings, while it behaves isotherm, yet decreasing in temperature. This is a new type of expansion that I therefore coin: **Supertropic Expansion**

The definition of it is: "an adiabatic, non-isentropic expansion"

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**We can now design a PV-diagram**

(as if it were about a real gas!)

For comparison, we do the same for an isotherm process, where \( \kappa = 1 \)

$$P_{\lambda} = P_1 \left( \frac{v_1}{v_{\lambda}} \right)^n \cdot 10^{-5}$$

$$W_{fp} := P_1 \cdot v_1 \cdot 10^{-3} \quad W_t := W + W_{fp}$$

As Watt observed!

Indeed a fully isotherm process, although the temperature decreases during expansion. This means the expanding steam received as much heat from the charged water, as it did work.

A fully, i.e. ideal isotherm process, has never been achieved, considered impossible, due to irreversibilities occurring when heat from an external source is applied during expansion of a medium (like in the Sterling cycle process). James Watt did it and this has never been observed!

The explanation for this isotherm behavior simply is that the water molecules during expansion, while evaporating, remain in the saturated condition all the time, which means zero temperature gradients between the equally saturated gaseous molecules and thus no irreversibilities. The charge water is an internal heat source! We can see this with an entropy calculation:

$$S_{1w} := 1.3028 \quad S_{2w} := 0.8933 \quad \text{entropy of saturated water from steam table, in kJ/(kg K)}$$

$$S_{1s} := 7.36 \quad \text{and} \quad S_{2s} := 7.83 \quad \text{entropy of saturated steam from steam table, in kJ/(kg K)}$$

The entropy difference for the steam part: $$S_{2s} \cdot x_2 - S_{1s} \cdot x_1 = 0.32$$
If Watt would have had an ideal machine, no water in the charge and no leakage over the piston, so $x_1 = 1$, and we calculate the volume ratio ($V_r$), the above equations give the following result:

$$
\begin{pmatrix}
    n & \kappa \\
    v_1 & v_2 \\
    V_r & W \\
    x_1 & x_2 \\
\end{pmatrix}
\begin{pmatrix}
    1.12 \\
    1.12 \\
    1.69 \\
    5.84 \\
    3.45 \\
    194.72 \\
    1.00 \\
    0.94 \\
\end{pmatrix}

W_{fp} := P_1 \cdot v_1 \cdot 10^{-3} \quad W_t := W + W_{fp}

Work relationships

\[
\frac{W}{W_{fp}} = 1.15 \quad \frac{W_t}{W_{fp}} = 2.15
\]

Also then $n = \kappa$, thus an adiabatic process and the expansion is still close to isotherm, but we also see that the work done is around three times more than what Watt got out of his machine, with water in the charge. Had he had a high-efficiency machine that we can make today, the development of steam technology would have followed a different path!

With the technology of his days, Watt would have had to double the cylinder size for the same work as done under full pressure, which was not feasible. As a result, the expansive power of steam was never used, so Watt's, and all later steam engines, worked under full pressure.

With modern technology, the cylinder size would be more or less the same, because as we can see, the volumity in the ideal case is also around three times larger than the work done with Watt's technology, so the volume/work ratio would be close to 1, and at a lower volume ratio.

The entropy difference between the end and the start condition of the steam is:

$$
S_{2s} \cdot x_2 + \left(1 - x_2\right) S_{2w} - S_{1s} = -4.4 \quad \text{(which is a very large change, but ideal case - see below!)}
$$

An isotherm expansion (external heat applied) would have shown a positive change of entropy, thus we clearly have a "weird" type of expansion here: supertropic expansion, though it does not behave fully isotherm (because more molecules get liquefied than re-evaporated).

In the logPH-diagram it shows as follows:

Condensing a saturated vapor with volumity $V_1$ in point 1, at constant pressure $P_1$, by cooling off the heat $\Delta H_1$, and then expanded freely through an expansion valve, to point 3 at pressure $P_2$ and volumity $V_2$, is equivalent to isentropic expansion, directly from point 1 to 3, while doing the same work of the change of enthalpy $\Delta H_1$. Because no heat is exchanged with the surroundings, it is an adiabatic process also.

That's all very well for real gases, but NOT so for saturated vapors. Through the supertropic effect, the fluid expands to pressure $P_3$ in point 4, doing the greater work $\Delta H_2$, while a negative change of entropy results.
In the graph left, a saturated vapor expands supertropically from $V_1, P_1$ in point 1 to $V_2, P_2$ in point 2, doing the expansion work $W_{\text{exp}}$.

In point 2, most of the liquid molecules have combined to liquid droplets, wetting the inside surfaces of the expander.

This liquid has a bad heat exchange contact with the gaseous molecules and so during (fast) compression, from point 2 to the original volumity in point 3, due to the temperature gradients arising, this liquid at best can become saturated and the quality $x$ remains constant. In practice however, slugging of liquid molecules (reciprocating pistons) can cause some superheat (point 3 shifts towards point 1).

If the compression follows the x-line for constant quality, the compression work $W_{\text{cp}}$ is clearly less than the previous expansion work. To close the cycle in point 1, heat $Q$ must be absorbed from the surroundings and the equivalent energy appears as mechanical work on the shaft.

\textit{Mind that this would even be true if the expansion was isentropic, just at a smaller difference between the expansion and the compression work! (see former graph, from point 3 along $x_1$)}

\textbf{If the used medium is a refrigerant, the whole cycle can work below ambient temperature and thus we have a concept here to convert ambient heat into mechanical energy, while having a chiller at the same time!}

Absorbing heat from the surroundings decreases the entropy of it, so is this a "negative" entropy machine? No, because the entropy of the machine increases with the same amount from point 3 to 1, so its change of entropy is zero. The mechanical work it gives off to a user, finally becomes heat at ambient temperature again, increasing the entropy of the surroundings, thus canceling out the entropy decrease at the cold side of the machine. Note that it doesn't have a warm side. Instead of cooling, mechanical work is delivered, thus getting around the Kelvin statement! Hence, the total change of surroundings and system remains zero, in compliance with the Second Law of Thermodynamics for fully reversible processes.

In practice however, there will be so called "irreversibilities", aka "losses", due to internal friction, leakage, etc, thus causing added entropy, and so the output power will be less than in the ideal, fully reversible case. Clausius' formulation of the Second Law would apparently forbid that heat can flow from a colder to a warmer region, BUT that is without side effects occurring, as he stated. The said irreversibilities however, ARE such side effects! Moreover, it happens spontaneously, which complies with Ludwig Boltzmann's definition of the Second Law, by which the change of entropy is zero, IF the probability for the process (its micro-states) to occur spontaneously, is 100%. There is thus no conflict with classical thermodynamics.

Mind that whenever the talk is about "negative entropy machines", the advocates of it lack basic knowledge in thermo-physics. Apropos that; entropy is a measure for the dispersion of energy, as follows from Clausius’ $\Delta S = \Delta Q_{\text{rev}}/T$. There is nothing about disorder of particles in that notation. Confusion arises as to Boltzmann's "probability for micro-states", which seems to relate to the disorder of particles. However, it is the probability that accounts for entropy change, not the micro-states themselves. This also follows from the notation: $\Delta S = k \cdot \ln(W_2/W_1)$, where $W$ stands for "Wahrscheinlichkeit", which is German for "probability".