5. Second Law of Thermodynamics

First law: $\oint \partial Q = \oint \partial W$ for a cyclic process

Questions: 1. Which direction?

2. Can any cycle really happen?

Second Law: Processes proceed in a certain direction only

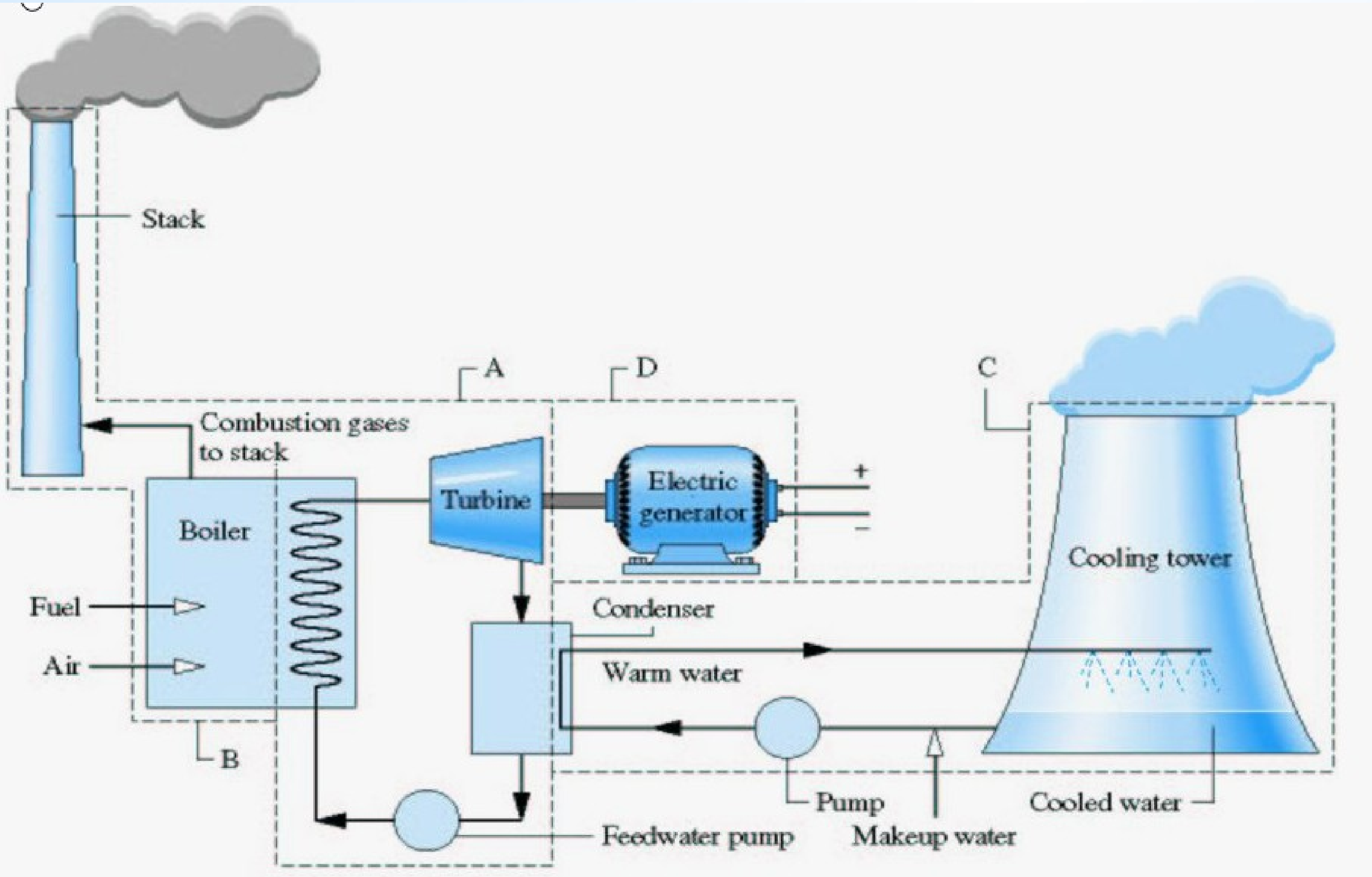
5.1 Heat Engines and Refrigerators

Heat Engine: A machine which reverses net heat (+) form the surroundings and does net work (+) on the surroundings (usually in a cyclic process)

Working fluid: The substance to or from which heat is transfered

Observation: Heat always flows from a high temperature to a low temperature region

The most important heat engine operating on a cycle is the steam power plant.



ME – 351 THERMODYNAMICS OF HEAT POWER

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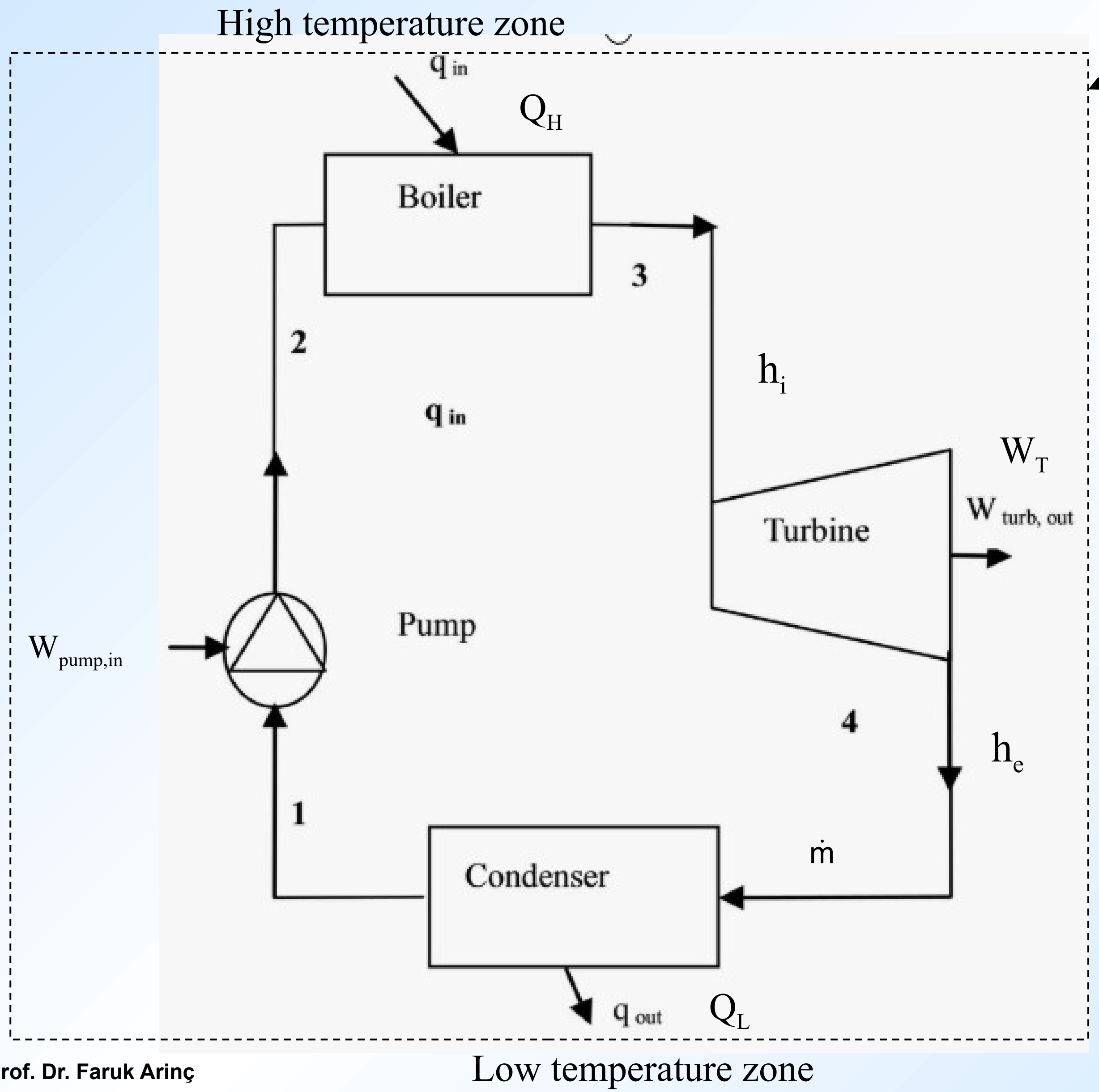
Fall 1995



$\dot{Q}_H > \dot{Q}_L$, so net heat is +

$$\dot{W}_T = m\,(h_i - h_e)$$
$$= \dot{Q}_H - \dot{Q}_L$$

Define efficiency:

$$\eta = \frac{\text{Useful output}}{\text{Input energy}} = \frac{\dot{W}_T}{\dot{Q}_H}$$

$$\eta = \frac{\dot{Q}_H - \dot{Q}_L}{\dot{Q}_L} = 1 - \frac{\dot{Q}_L}{\dot{Q}_H}$$

Question: $Q_L = 0$

$\eta = 1$ or 100 %

Is it possible?

Refrigerator: It is the same machine as the heat engine, except that it receives work (-) from the surroundings and transfers (pumps) heat from from a low temperature zone to a high temperature zone. The objective is to cool the low temperature zone.

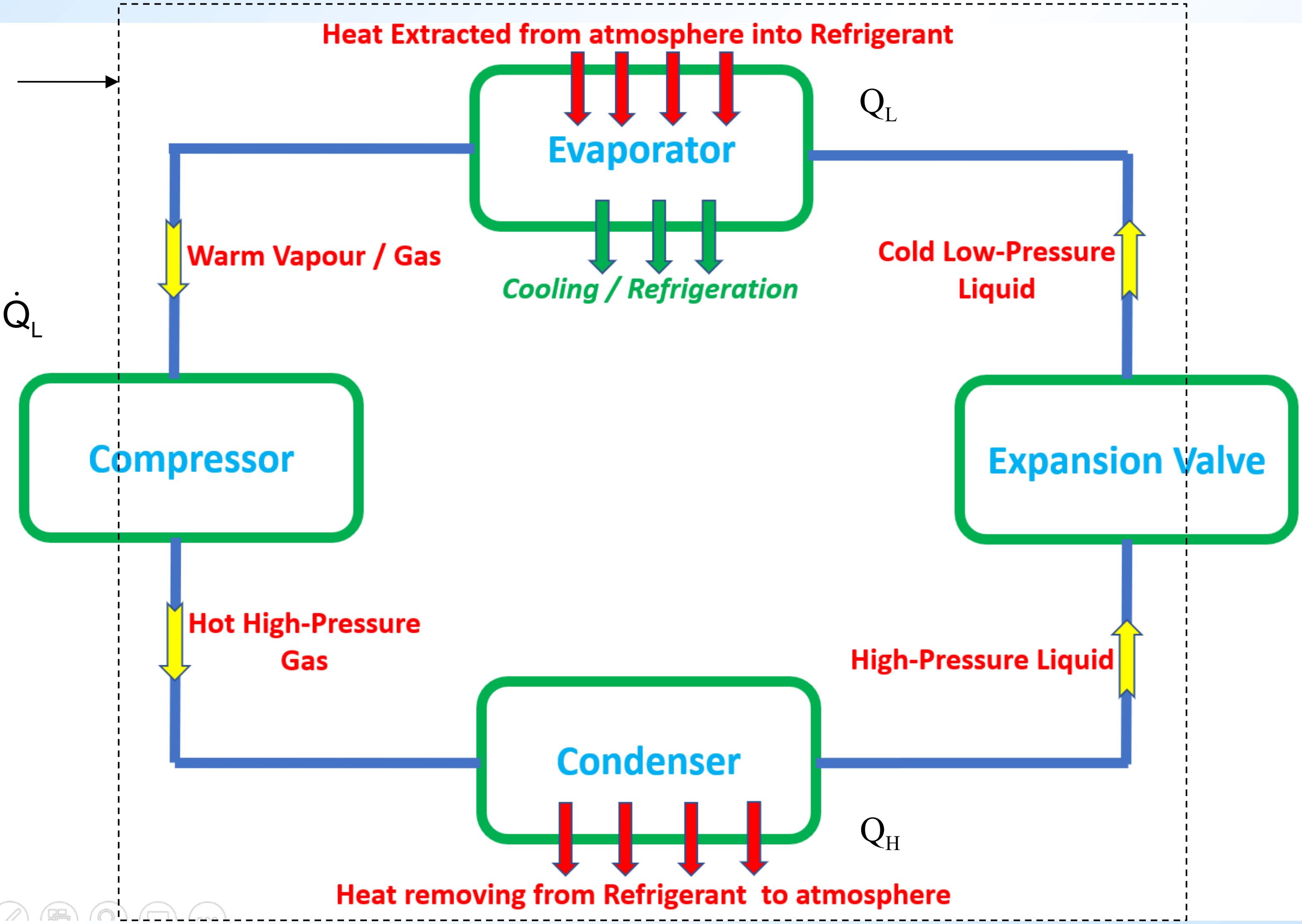
Heat Pump: Same as the refrigerator. The objective is to heat the high temperature zone.

Define: Thermal Resevoir: It is a zone wehere heat can be transfered indefinitely wihout temperature change

Low temperature zone

System boundary

$$\dot{W}_T = \dot{Q}_H - \dot{Q}_L$$



Heat Extracted from atmosphere into Refrigerant

Q_L

Evaporator

Warm Vapour / Gas

Cooling / Refrigeration

Cold Low-Pressure Liquid

Compressor

Expansion Valve

Hot High-Pressure Gas

High-Pressure Liquid

Condenser

Q_H

Heat removing from Refrigerant to atmosphere

High temperature zone

Define: Coefficient of Performance (COP): $\beta = \dfrac{\text{Useful output}}{\text{Input energy}}$

Refrigerator: $$\beta = \frac{\dot{Q}_L}{\dot{W}} = \frac{\dot{Q}_L}{\dot{Q}_H - \dot{Q}_L} = \frac{1}{\dot{Q}_H / \dot{Q}_L - 1}$$

Heat Pump: $$\beta = \frac{\dot{Q}_H}{\dot{W}} = \frac{\dot{Q}_H}{\dot{Q}_H - \dot{Q}_L} = \frac{1}{1 - \dot{Q}_L / \dot{Q}_H}$$

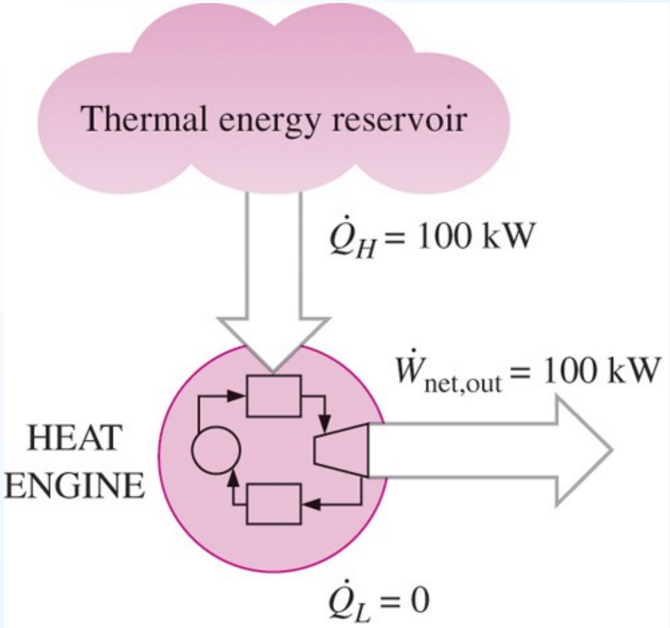
Question: Can ve have $\dot{Q}_H = \dot{Q}_L$ or $\dot{W} = 0$ so that $\beta = 0$?

5.2 The Second Law

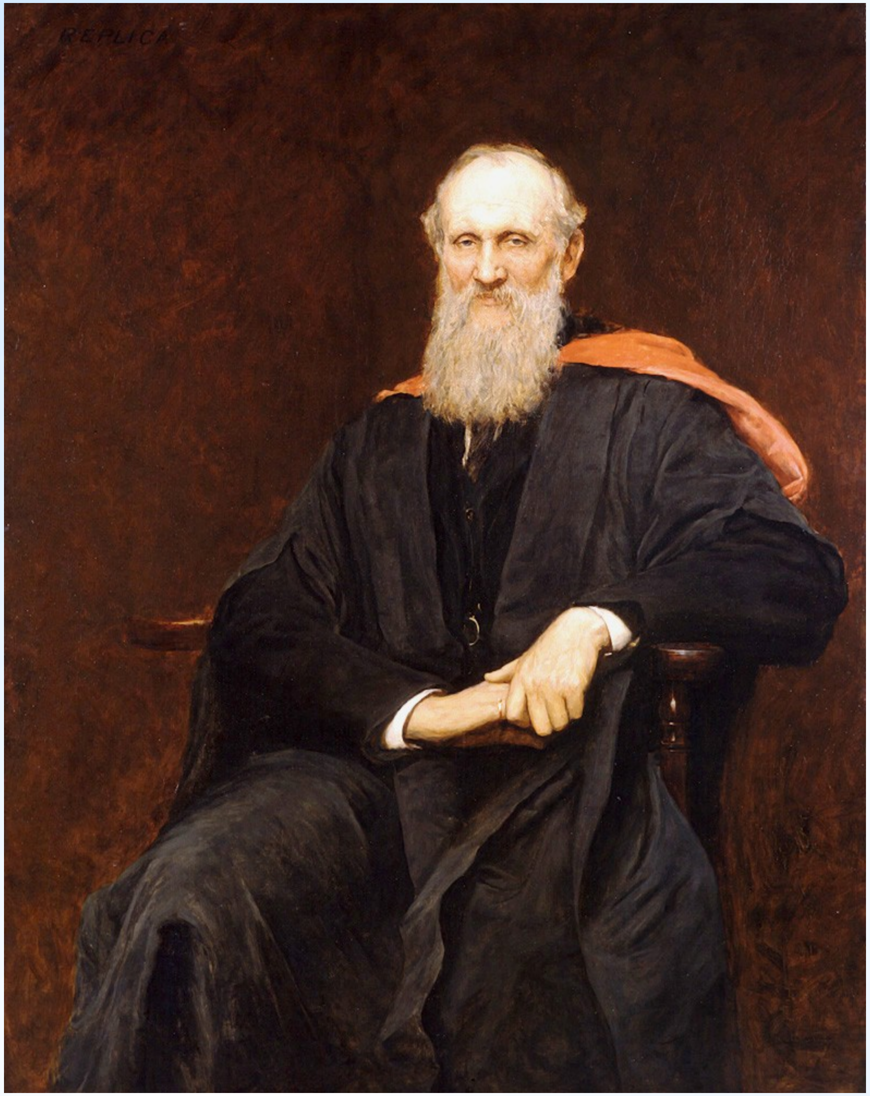
There are several ways in which the second law of thermodynamics can be stated. Listed below are three that are often encountered. Altough the three may not appear to have much connection with each other, **they are equivalent**.

Kelvin-Planck statement:

No process is possible whose **sole** result is the absorption of heat from a reservoir and the conversion of this heat into work.



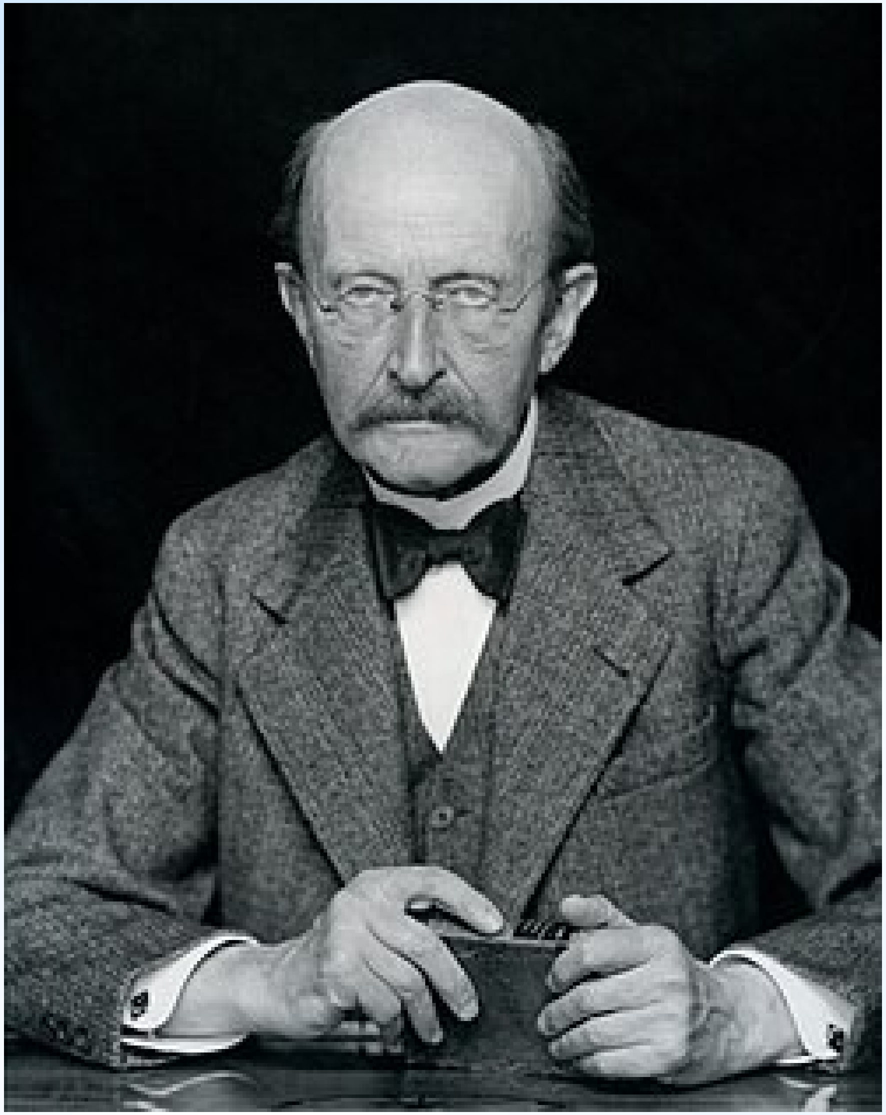
This is not possible



William Thomson (Lord Kelvin)

British Mathematician

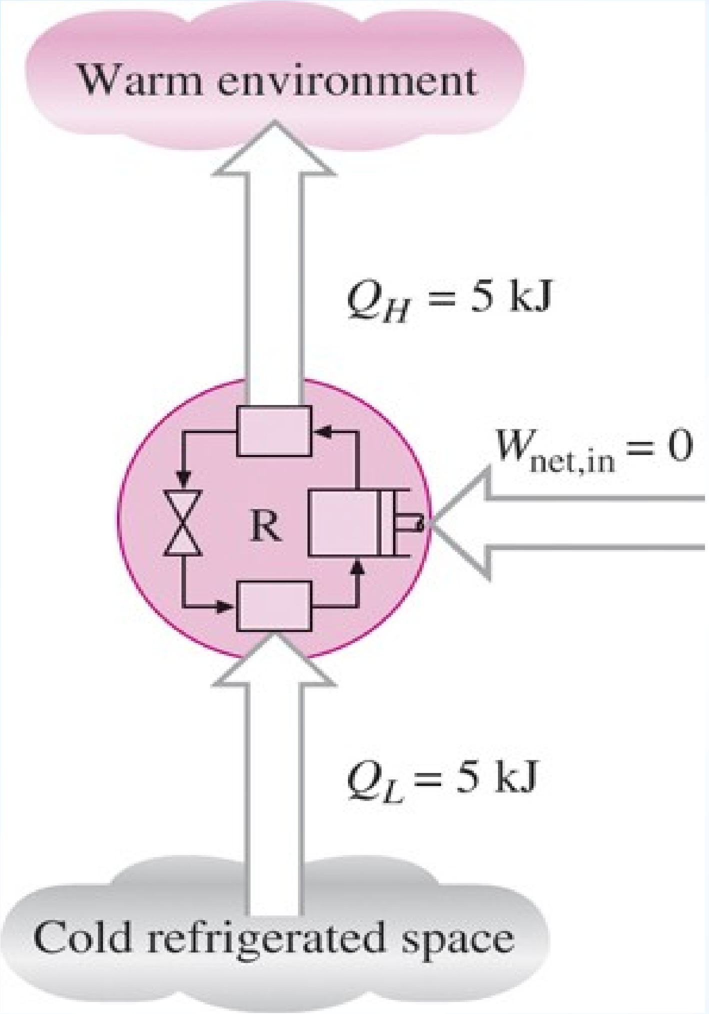
1824 - 1907



Max Karl Ernst Ludwig Planck

German Physicist

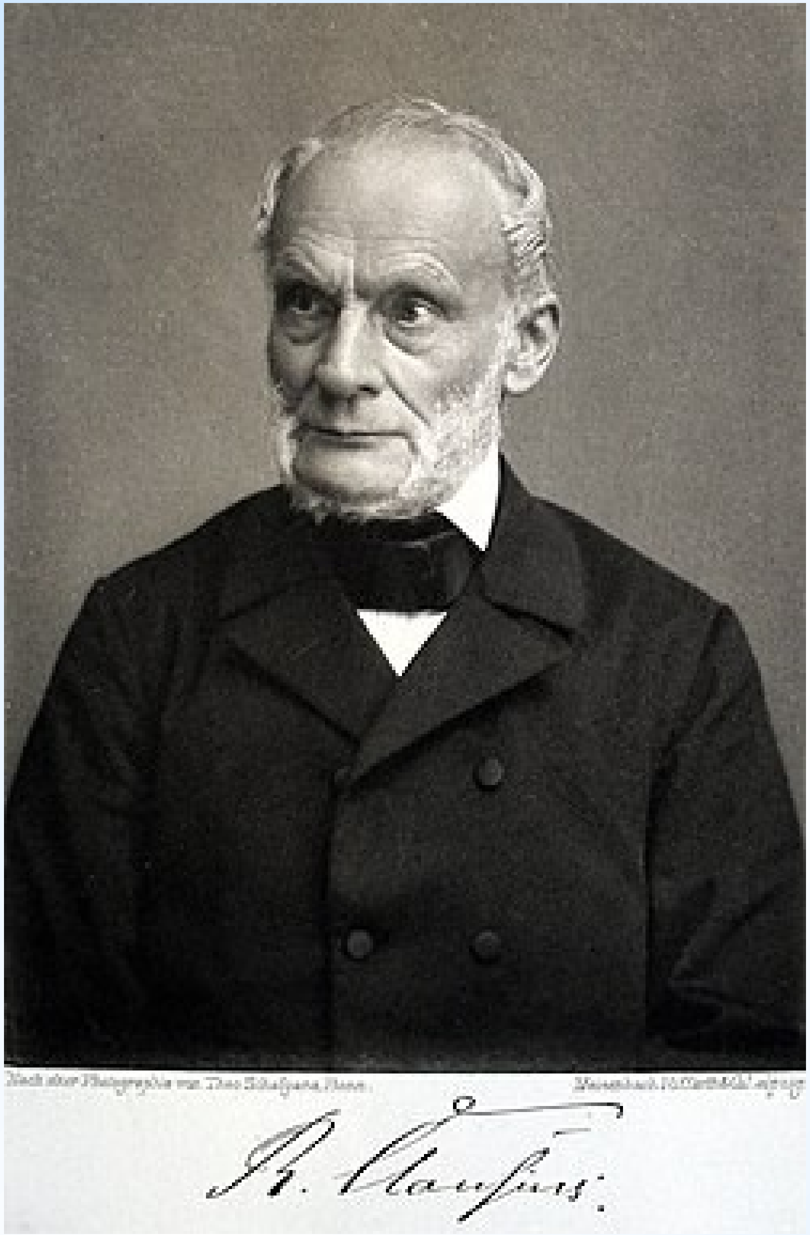
1858 - 1947



Clausius statement:

No process is possible whose **sole** result is the transfer of heat from a cooler to a hotter body.

$T_1 > T_2$



Rudolf Julius Emanuel Clausius

German Physicist

1822 - 1888

These two statements answer our two previous questions.

First law: $\oint \partial Q = \oint \partial W$ for a cyclic process

Questions: 1. Which direction?

2. Can any cycle really happen?

Second Law: Processes proceed in a certain direction only

Three observations:

1. Both are negative statements. So, it is impossible to prove them except experientally.

2. These two statements are equivalent

3. It is impossible to construct a perpetual motion machine of the second kind. (The first one violates the first law – create work from nothing)

5.3 Reversible Process

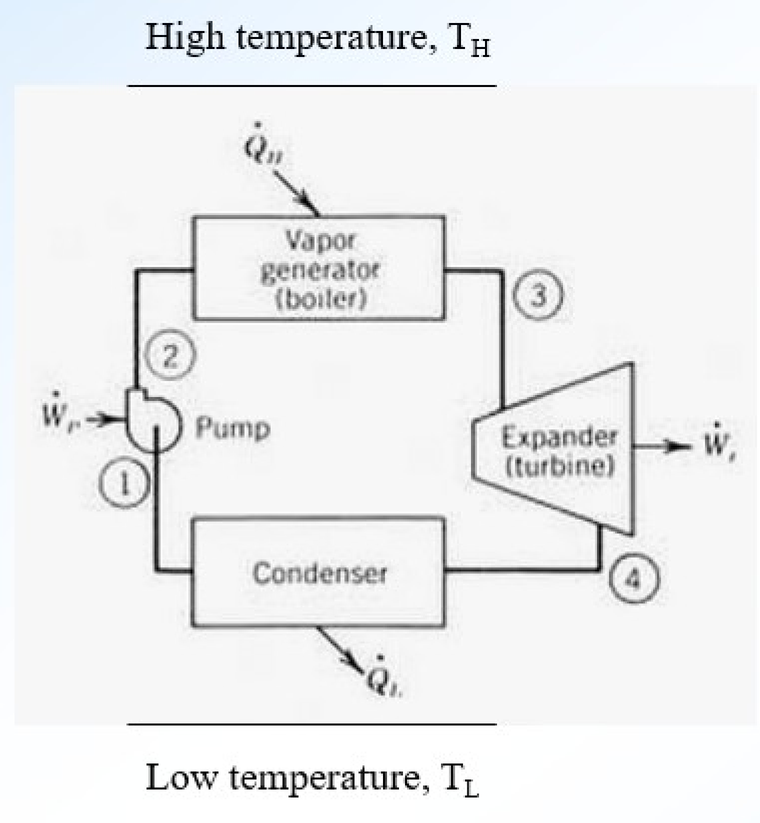
Definition: A reversible process for a system is defined as a process in which, once has taken place, can be reversed, and in doing so, leave no change in either the system or the surroundings.

Note that quasi-equilibrium process is a reversible process.

Factors that render a process reversible:

1. Friction
2. Unstrained expansion (remove a membrane)
3. Heat transfer through a finite temperature difference
4. Mixing two different substances
5. Others

5.4 Carnot Cycle



Question: In a heat engine (Rankine cycle shown in the Figure), how high the efficiency η can be if not 100 % (or β, coefficient of performance, for a refrigeration cycle)?

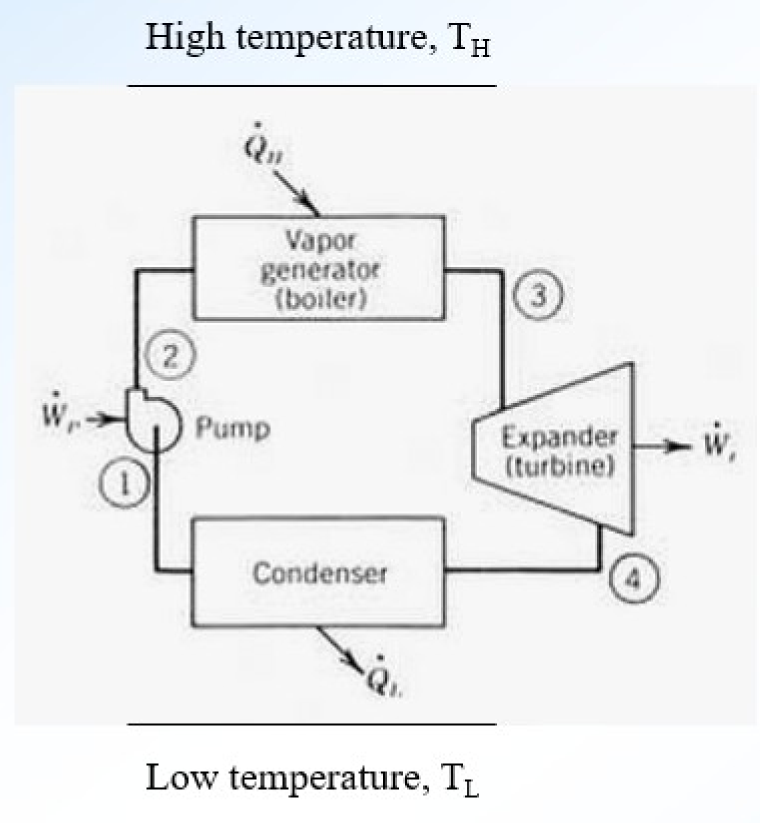
Sadi Carnot (a French scientist and an army officer) stated the 2nd law in 1824.

Heat always flows spontaneously from hotter to colder regions of matter (or 'downhill' in terms of the temperature gradient). Another statement is: "Not all heat can be converted into work in a cyclic process."

Nicolas Léonard Sadi Carnot

French Physicist

1796 - 1832



All the processes shown in the Figure (heat engine) are assumed to be reversible.

Boiler: Fluid boils or evaporates

Isothermal (constant T) process

Turbine: Adiabatic Process ; Q = 0

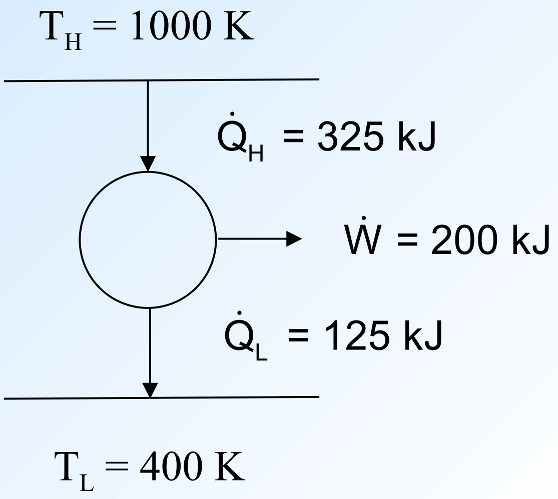
Condensor : Isothermal (constant T) process

Pump: Adiabatic Process ; Q = 0

Then: $\eta_C = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$

This (Carnot efficiency) is the maximum possible efficiency of a heat engine under ideal (reversible) conditions

Example



$T_H = 1000$ K

$\dot{Q}_H = 325$ kJ

$\dot{W} = 200$ kJ

$\dot{Q}_L = 125$ kJ

$T_L = 400$ K

$$\dot{W} = Q_H - Q_L = 325 - 125 = 200 \text{ kJ}$$

First law says check

$$\eta_C = 1 - \frac{T_L}{T_H} = 1 - \frac{400}{1000} = 0.75$$

$$\dot{W}_{max} = \eta_C \, \dot{Q}_H = (0.75)\,(325) = 195 \text{ kJ}$$

W = 200 kJ is impossible

Second law says impossible

5.5 Entropy

Rudolph Clasius was a German physicist and mathematician and is considered one of the central founding fathers of the science of thermodynamics. By his restatement of Sadi Carnot's principle known as the Carnot cycle, he gave the theory of heat a truer and sounder basis.

His most important paper, "On the Moving Force of Heat", published in 1850, first stated the basic ideas of the second law of thermodynamics

In 1865, he introduced the concept of entropy.

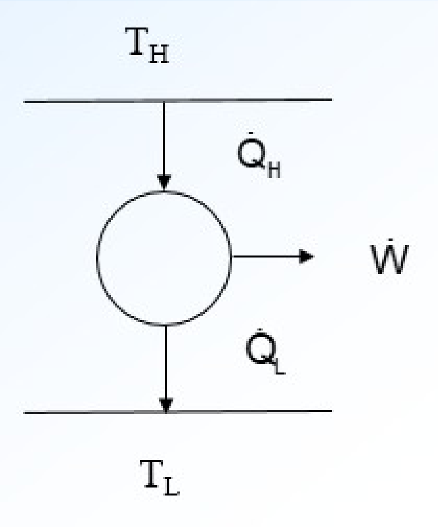
He defined it as the quotient of an infinitesimal amount of heat to the instantaneous temperature. He initially described it as *transformation-content*, in German *Verwandlungsinhalt*, and later coined the term *entropy* from a Greek word for *transformation*..

Entropy is a scientific concept, most commonly associated with states of disorder, randomness, or uncertainty.

The term and the concept are used in diverse fields, from classical thermodynamics, where it was first recognized, to the microscopic description of nature in statistical physics, and to the principles of information theory.

It has found far-ranging applications in chemistry and physics, in biological systems and their relation to life, in cosmology, economics, sociology, weather science, climate change and information systems including the transmission of information in telecommunication.

Clasius inequality: $\oint \frac{\delta Q}{T} \leq 0$ For the proof, consider a Carnot cycle:



$$\dot{W}_{max} = \dot{Q}_H - \dot{Q}_L \quad , \quad \dot{Q}_L \neq 0$$

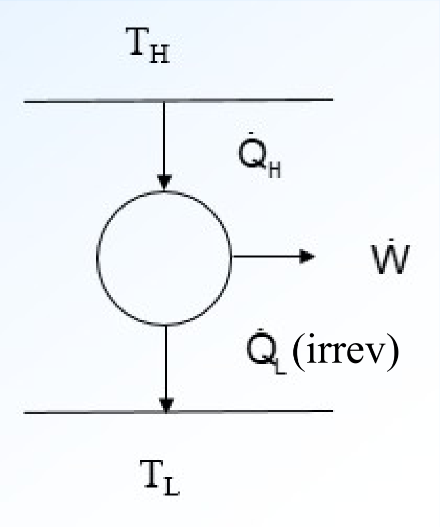
$$\left.\begin{array}{l} \oint \delta W = Q_H - Q_L \\ \oint \delta Q = \oint \delta W \quad \text{First Law} \end{array}\right\} \begin{array}{l} \oint \delta Q = Q_H - Q_L \\ \dot{Q}_H - \dot{Q}_L > 0 \end{array}$$

Therefore: $\oint \delta Q > 0$

Also $\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$ since $\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$ for a Carnot cycle

Therefore: $\oint \frac{\delta Q}{T} = 0$ for a reversible (Carnot) cycle

Consider an irreversible (real) cycle:



$Q_{L,\,\mathrm{irrev}} > Q_{L,\mathrm{rev}}$ since $\eta_{\mathrm{irrev}} < \eta_{\mathrm{rev}}$

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} < 0 \quad \text{for an irreversible cycle}$$

$$\boxed{\oint \frac{\delta Q}{T} < 0 \quad \text{for an irreversible cycle}}$$

One can also prove that the same is true for refrigeration cycles.

The quantity $\oint \frac{\delta Q}{T}$ is given the special name of «entropy»

$\oint \frac{\delta Q}{T} = dS$ only if the process is reversible, independent of the path

Clasius inequality: $\oint \frac{\delta Q}{T} \leq 0$

Reversible cycle: $\oint \frac{\delta Q}{T} = 0$

Reversible process: $\frac{\delta Q}{T} = dS$

$$\int_1^2 \frac{\delta Q}{T} = S_2 - S_1$$

Irreversible cycle: $\oint \frac{\delta Q}{T} < 0$

Impossible cycle: $\oint \frac{\delta Q}{T} > 0$

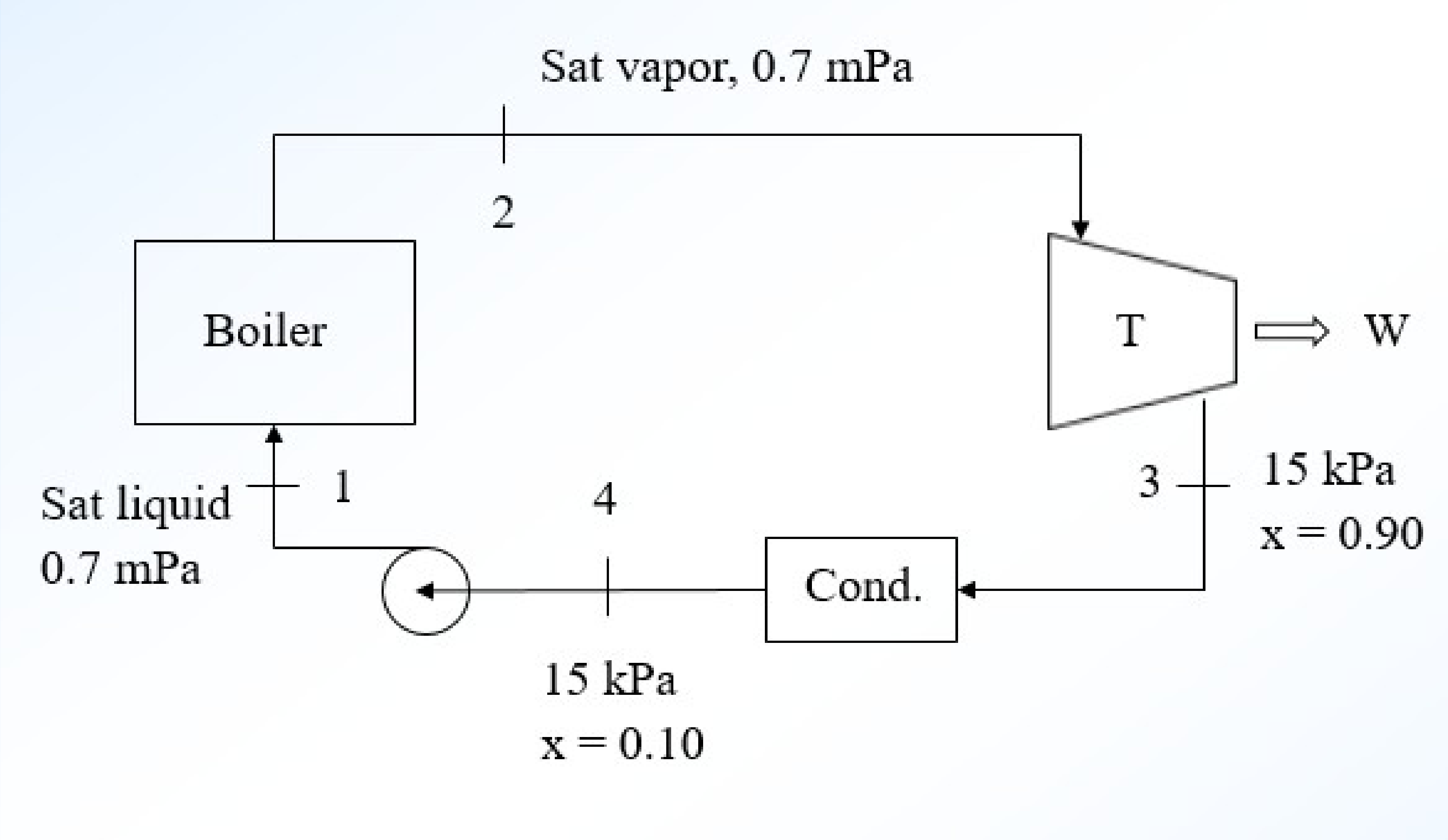
Irreversible process: $\frac{\delta Q}{T} \neq dS$

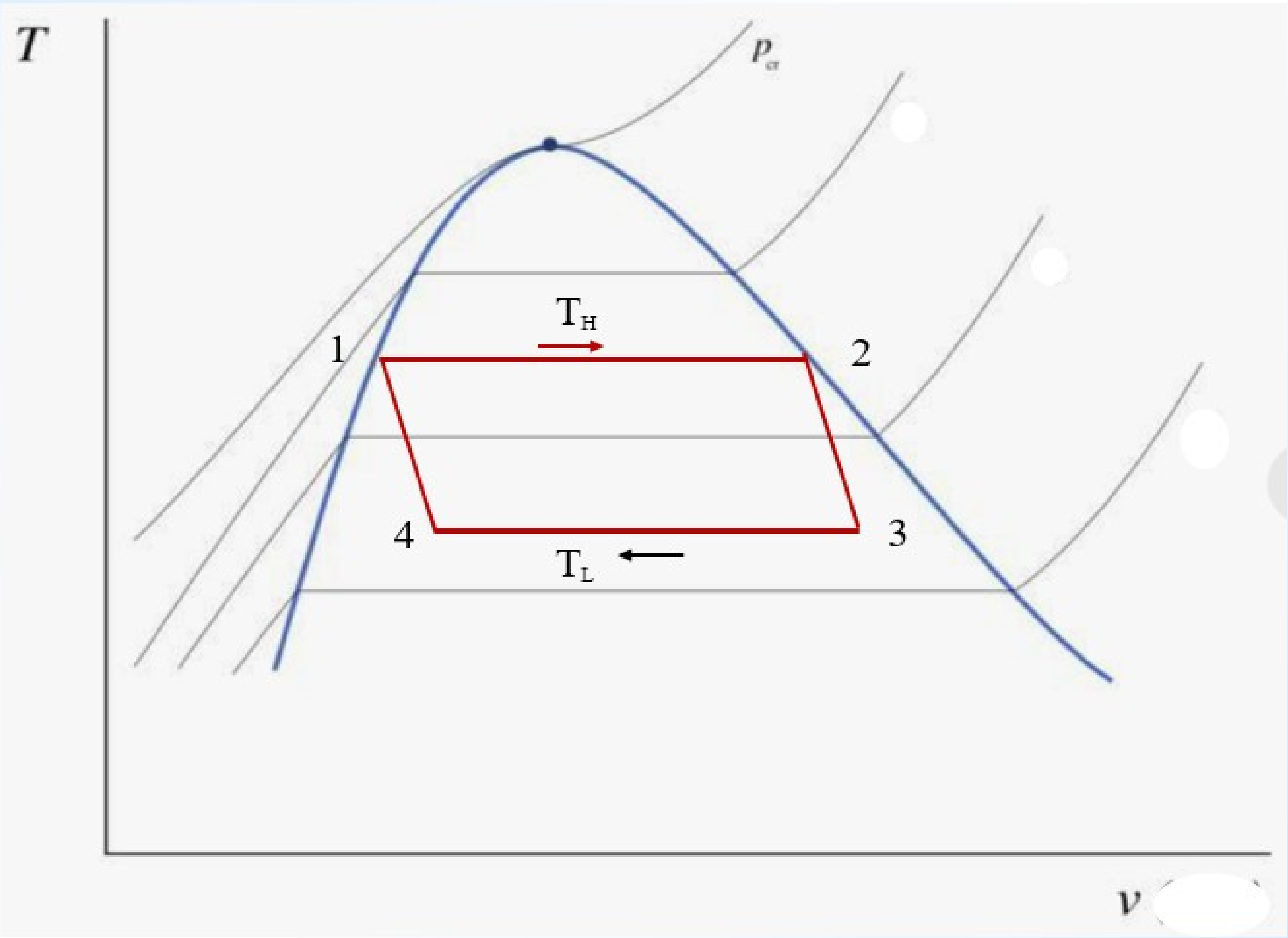
$$\int_1^2 \frac{\delta Q}{T} \neq S_2 - S_1$$

Entropy (S, in kJ/K) is a measure of orderliness in the system.

It is a property of a system independent of the path of a process.

Example


Sat vapor, 0.7 mPa
2
Boiler
T
W
Sat liquid
0.7 mPa
1
4
3
15 kPa
x = 0.90
Cond.
15 kPa
x = 0.10


T
P_{cr}
T_H
1
2
3
4
T_L
v

$$\oint \frac{\delta Q}{T} = \int \left(\frac{\delta Q}{T} \right)_{\text{Boiler}} + \int \left(\frac{\delta Q}{T} \right)_{\text{Cond.}} = \frac{1}{T_H} \int_1^2 \delta Q + \frac{1}{T_L} \int_3^4 \delta Q = \frac{{}_1Q_2}{T_H} + \frac{{}_3Q_4}{T_L}$$

$${}_1Q_2 = m \left(h_2 - h_1 \right) \quad \text{and} \quad {}_3Q_4 = m \left(h_4 - h_3 \right)$$

Find the enthalpies at states 1, 2, 3, and 4 using the steam table.

$$\left.\begin{array}{l} \text{At } P_1 = P_2 = 0.7 \text{ MPa} \\ \text{Saturated vapor} \end{array}\right\} \left.\begin{array}{l} T_2 = T_H = 164.97\ ^\circ\text{C} \\ h_2 - h_1 = 2066.3 \text{ kJ/kg} \end{array}\right\} \ {}_1Q_2 = 2066.3 \text{ m kJ}$$

$$\left.\begin{array}{l} \text{At } P_3 = P_4 = 15 \text{ kPa} \\ \text{Saturated liquid} \end{array}\right\} \left.\begin{array}{l} T_4 = T_L = 53.97\ ^\circ\text{C} \\ h_4 - h_3 = -\ 1898.4 \text{ kJ/kg} \end{array}\right\} \ {}_3Q_4 = -\ 1898.4 \text{ m kJ}$$

$$\oint \frac{\delta Q}{T} = \frac{{}_1Q_2}{T_H} + \frac{{}_3Q_4}{T_L} = \frac{2066.3\ \text{m}}{(164.97 + 273)} + \frac{-\ 1898.4\ \text{m}}{(53.97 + 273)} = -\ 1.087\ \text{m}$$

$\oint \frac{\delta Q}{T} \neq 0$ indicates that it is not a Carnot cycle.

$\oint \frac{\delta Q}{T} < 0$ indicates that the second law is obeyed.

This example shows that for a cyclic irreversible (real) process $\oint \frac{\delta Q}{T} < 0$

For a irreversible (real) process $\boxed{\frac{\delta Q}{T} < dS}$ Clasius inequality

In the previous example problem, either the process 2 to 3 or 3 to 4 or both are irreversible (due to friction, probably).

Entropy, S, in kJ/K, is an extensive property.

Specific entropy, $s = S / m$, in kJ/kg.K, is an intensive property.

In the two-phase region:

$$\left.\begin{aligned} s &= (1 - x)\, s_f + x\, s_g \\ s &= s_f + x\, s_{fg} \\ s &= s_g - (1 - x)\, s_{fg} \end{aligned}\right\} \quad \text{Similar to v, h, and u}$$

See the thermodynamic (steam) tables for specific entropy.

Example

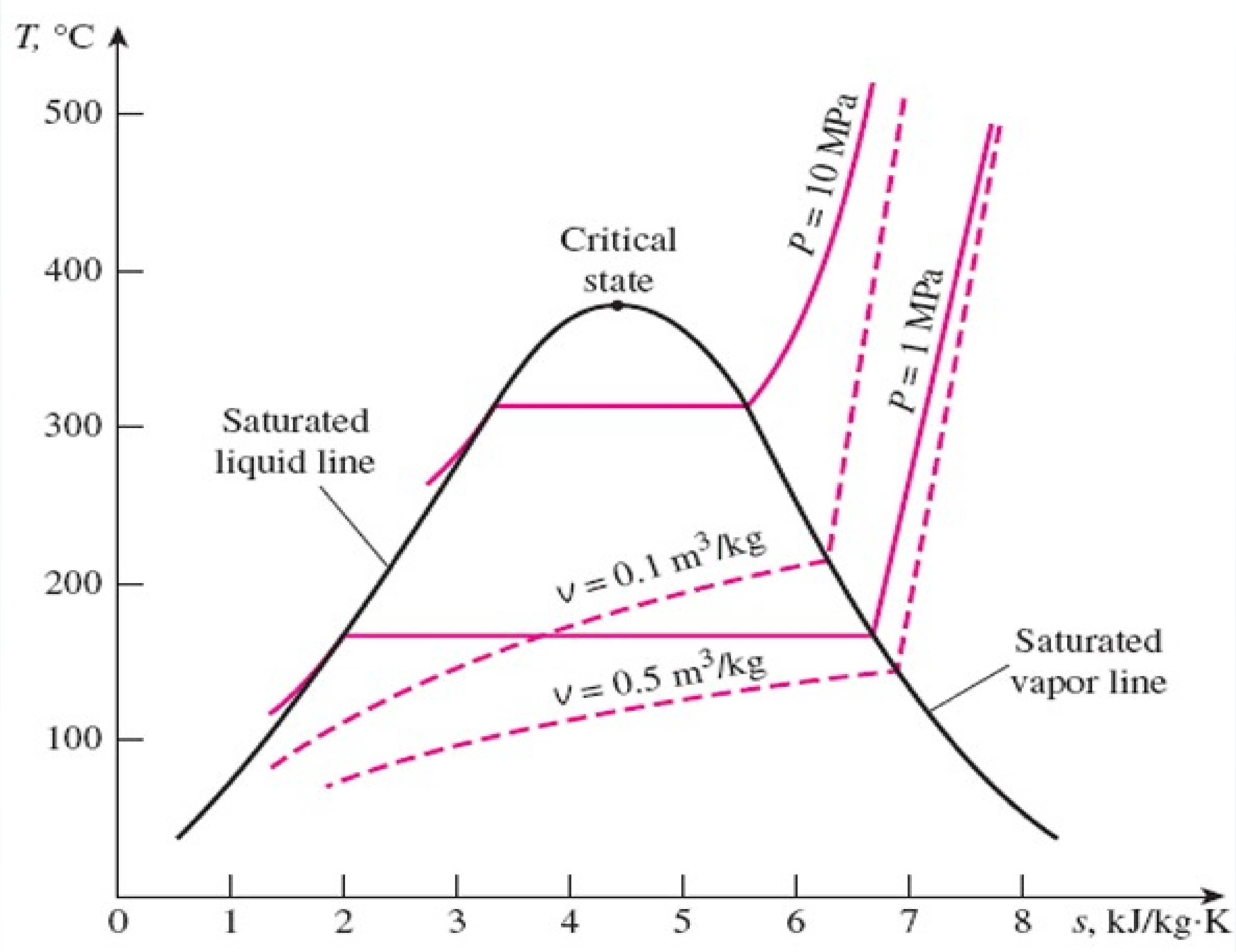
An inventor reports that he has a refrigeration compressor thet receives saturated Freon-12 vapor at -15 °C (s_g = 0.7046 kJ/kg.K) and delivers the vapor at 1 MPa and 50 °C. The compression process is adiabatic. Evaluate the report.

Solution

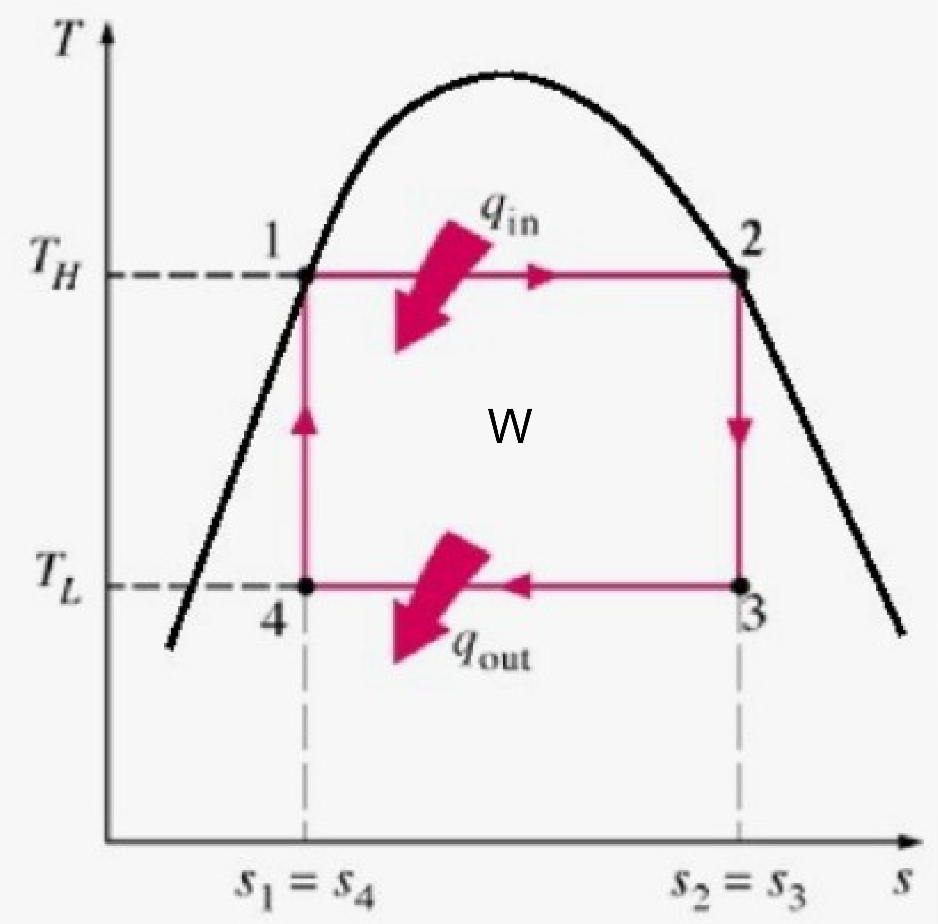
Adiabatic means $Q = 0$ Therefore, $s_2 - s_1 = 0$ if the process is reversible (ideal)

$s_2 > s_1$ if the process is irreversible (real)

$$\left.\begin{array}{l} \text{Properties of Freon-12: } s_1 = s_g = 0.7046 \text{ kJ/kg.K} \\ s_2 = 0.7021 \text{ kJ/kg.K} \end{array}\right\} \begin{array}{l} s_2 < s_1 \text{ Impossible} \\ \text{Reject the report} \end{array}$$


T, °C
500
400
300
200
100
0
1
2
3
4
5
6
7
8
s, kJ/kg·K
Critical state
Saturated liquid line
Saturated vapor line
P = 10 MPa
P = 1 MPa
v = 0.1 m³/kg
v = 0.5 m³/kg

Carnot cycle on a T-s diagram



1 – 2 Reversible, isothermal

$$_1Q_2 = Q_H = T_H \left(S_2 - S_1\right)$$

3 – 4 Reversible, isothermal

$$_3Q_4 = Q_L = T_L \left(S_3 - S_4\right)$$

2 – 3 Reversible, adiabatic

$$_2Q_3 = 0 \quad , \quad \Delta S = 0$$

4 – 1 Reversible, adiabatic

$$_4Q_1 = 0 \quad , \quad \Delta S = 0$$

$$W = W_{max} = Q_H - Q_L$$

$$= T_H \left(S_2 - S_1\right) + T_L \left(S_4 - S_3\right)$$

Corollary: Reversible, adiabatic processes are isentropic.

There are two difficulties with this cycle. We'll come to that.

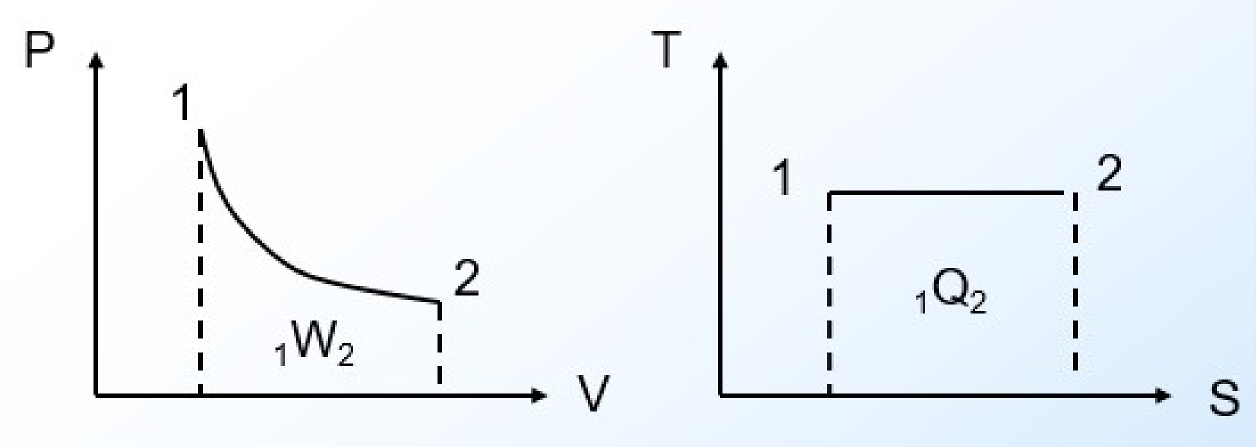
For a reversible process: $\delta Q = T\,ds$ and $\delta W = P\,dV$

First law: $\delta Q = dU + \delta W$

First law for a reversible process: $\boxed{T\,ds = dU + P\,dV}$

$$\left.\begin{array}{l} H = U + P\,V \\ dH = dU + P\,dV + V\,dP \end{array}\right\} \boxed{T\,ds = dH - V\,dP}$$

For a reversible process:



5.6 Entropy Change for an Ideal Gas

Ideal gas law: $P\,V = m\,R\,T$ or $P\,v = R\,T$

Reversible process: $\dfrac{\delta Q}{m} = T\,ds = du + P\,dv$

$$\frac{\delta Q/m}{T} = ds = \frac{du}{T} + \frac{P}{T}\,dv = \frac{du}{T} + \frac{R}{v}\,dv$$

$$\left.\begin{aligned} du &= c_v\,dT \\ dh &= c_p\,dT \end{aligned}\right\}$$

For the definitions of c_v and c_p, see the previous problem

$$ds = \frac{c_v}{T}\,dT + \frac{R}{v}\,dv = \frac{c_p}{T}\,dT - \frac{R}{P}\,dP$$

Integrate

$$\int_1^2 ds = \int_1^2 \frac{c_v}{T}\, dT + \int_1^2 \frac{R}{v}\, dv = \int_1^2 \frac{c_p}{T}\, dT - \int_1^2 \frac{R}{P}\, dP$$

$$\boxed{s_2 - s_1 = \int_1^2 \frac{c_v}{T}\, dT + R \ln\left(\frac{v_2}{v_1}\right)}$$

$$\boxed{s_2 - s_1 = \int_1^2 \frac{c_p}{T}\, dT - R \ln\left(\frac{P_2}{P_1}\right)}$$

When c_v and c_p are constants:

$$\boxed{s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)}$$

$$\boxed{s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)}$$

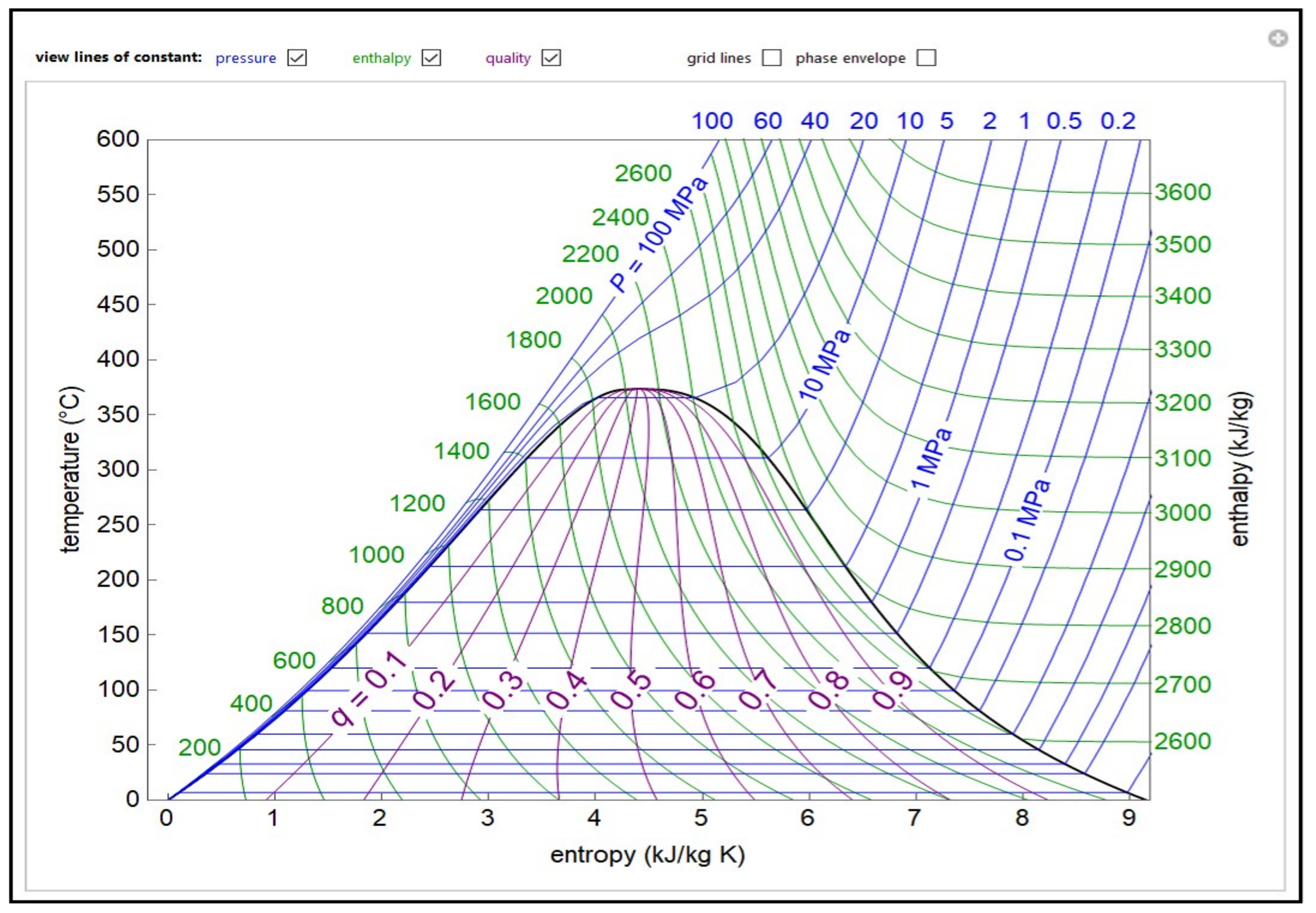
Compare these relations with those given in the textbook.

For an isothermal and reversible process ($T_2 = T_1 = T$):

$${}_1W_2 = m\,R\,T\,\ln\left(\frac{v_2}{v_1}\right) = m\,R\,T\,\ln\left(\frac{P_2}{P_1}\right)$$

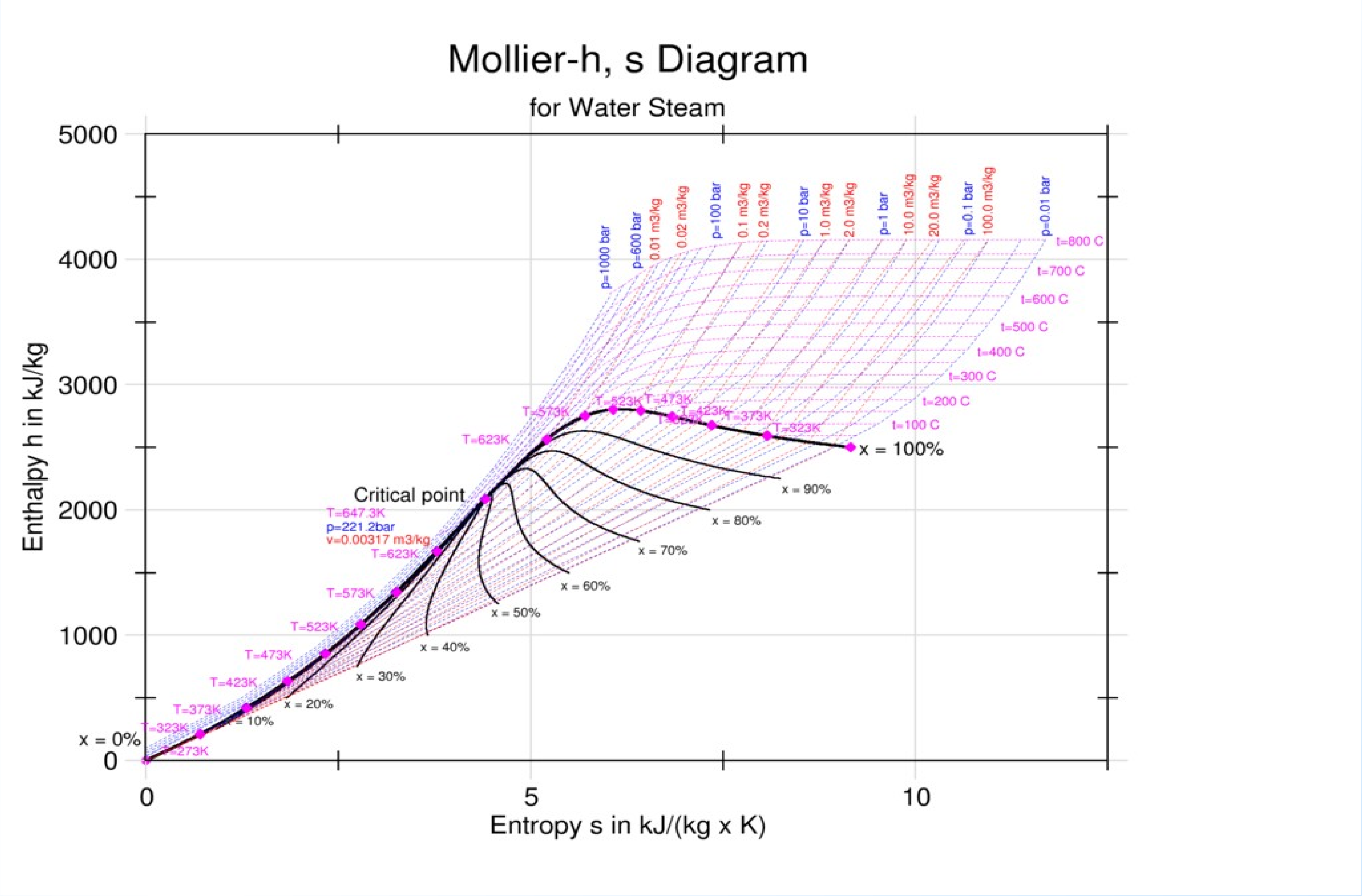
$${}_1Q_2 = \int_1^2 T\,ds = \int_1^2 dU + \int_1^2 P\,dV = P_1\,V_1\,\ln\left(\frac{v_2}{v_1}\right)$$

$${}_1Q_2 = m\,R\,T\,\ln\left(\frac{v_2}{v_1}\right)$$



view lines of constant: pressure ☑ enthalpy ☑ quality ☑ grid lines ☐ phase envelope ☐

T – s diagram for water


Mollier-h, s Diagram
for Water Steam
Enthalpy h in kJ/kg
Entropy s in kJ/(kg x K)
5000
4000
3000
2000
1000
0
0
5
10
p=1000 bar
p=600 bar
0.01 m3/kg
0.02 m3/kg
p=100 bar
0.1 m3/kg
0.2 m3/kg
p=10 bar
1.0 m3/kg
2.0 m3/kg
p=1 bar
10.0 m3/kg
20.0 m3/kg
p=0.1 bar
100.0 m3/kg
p=0.01 bar
t=800 C
t=700 C
t=600 C
t=500 C
t=400 C
t=300 C
t=200 C
t=100 C
Critical point
T=647.3K
p=221.2bar
v=0.00317 m3/kg
T=623K
T=573K
T=523K
T=473K
T=423K
T=373K
T=323K
T=273K
x = 0%
x = 10%
x = 20%
x = 30%
x = 40%
x = 50%
x = 60%
x = 70%
x = 80%
x = 90%
x = 100%