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# Thermodynamics and Statistical Mechanics

**Thermodynamics II**
*4 September 2014*

- Heat capacity
- Heat machines
- Second Law of Thermodynamics
- Carnot Theorem
- Clausius inequality
- Entropy

# HEAT CAPACITY

In most cases adding heat to system leads to increase of its $T$

Heat capacity ☛ $$C = \frac{\delta Q}{dT} \qquad (28)$$

Heat capacity is proportional to system size and so is extensive variable

Introduce specific quantities ☛ heat and heat capacity per kilomole

$$q \equiv \frac{Q}{n} \qquad c = \frac{C}{n} = \frac{\delta q}{dT} \qquad (29)$$

Heat capacity depends on the type of the process

# HEAT CAPACITY (isobaric and isochoric processes)

If heat is added to system while volume is kept constant $dV = 0$

we obtain the isochoric heat capacity $C_V = \left(\frac{\delta Q}{dT}\right)_V$ **(30)**

If we keep a constant pressure $dP = 0$

we obtain the isobaric heat capacity $C_P = \left(\frac{\delta Q}{dT}\right)_P$ **(31)**

In isochoric case no work is done

so heat fully converts into internal energy and temperature increases

In the isobaric case system usually expands upon heating

and a negative work is done on it

This leads to smaller increase of $U$ and thus smaller increase of $T$

# HEAT CAPACITY (isothermal and adiabatic processes)

In isothermal process system receives or lose heat but $dT = 0$

$$C_T = \pm\infty$$

In adiabatic process $\delta Q = 0$ but the temperature changes

$$C_S = 0$$

Subscript $S$ refers to entropy ☛ state function

conserved in reversible adiabatic processes

## ISOCHORIC HEAT CAPACITY

Let us rewrite first law of thermodynamics (25) with (17) in form

$$\delta Q = dU + PdV \quad (32)$$

Considering energy as a function of $T$ and $V$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (33)$$

Combining this with the previous equation

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \quad (34)$$

At constant volume this equation yields $\delta Q = (\partial U/\partial T)_V \, dT$ so

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (35)$$

# ISOBARIC HEAT CAPACITY

To find isobaric heat capacity $C_P$ we must take into account that at constant $P$ the $V$ in (32) changes because of thermal expansion,

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT$$

Inserting this into (34) we obtain

$$\delta Q = \left[C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT \qquad (37)$$

so

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad (38)$$

# MAYER'S RELATION

Because of of negligibly weak interaction between particles energy of ideal gas depends only on $T$ ☛ $(\partial U/\partial V)_T = 0$

From the equation of state (5) we obtain ☛ $(\partial V/\partial T)_V = nR/P$

Substituting these in (38) we obtain Mayer's relation for ideal gas

$$C_P = C_V + nR \tag{39}$$

or $c_P = c_V + R$ for heat capacities per kilomole

In terms of number of particles $N$ Mayer's relation becomes

$$C_P = C_V + N\,k_B \tag{40}$$

or $c_P = c_V + k_B$ for heat capacities per particle

# ADIABATIC PROCESS OF IDEAL GAS

For ideal gas internal energy is a function of temperature only

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V\, dT \qquad (44)$$

In adiabatic process $\delta Q = 0$

Substituting these two results in (25) and using (17) we obtain

$$C_V\, dT = -P dV \qquad (45)$$

Either $P$ or $V$ can be eliminated with help of (5)

$$C_V\, dT = -n\, RT\, \frac{dV}{V} \qquad (46)$$

This can be integrated if temperature dependence $C_V\,(T)$ is known

# PERFECT GAS

For perfect gas ☛ $C_V = \text{const}$ ➢ integration of (46) yields

$$\ln T = -\frac{nR}{C_V} \ln V + \text{const} \quad (47)$$

or equivalently $TV^{nR/C_V} = \text{const}$ (48)

it is convenient to introduce $\gamma \equiv \frac{C_P}{C_V}$ (49)

with help of Mayer's relation (39)

$$C_V = \frac{nR}{\gamma - 1} \qquad C_P = \frac{nR\gamma}{\gamma - 1} \quad (50)$$

Adiabatic equation (48) becomes ☛ $TV^{\gamma-1} = \text{const}$ (51)

Using (5) we can rewrite (51) as $PV^{\gamma} = \text{const}$ (52)

or else as $TP^{1/\gamma-1} = \text{const}$ (53)

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# WORK DONE IN ADIABATIC PROCESS

Using (52)

$$W_{12} = \int_{V_1}^{V_2} P\, dV = \text{const} \int_{V_1}^{V_2} \frac{dV}{V} = \frac{1}{1-\gamma}(V_2^{1-\gamma} - V_1^{1-\gamma}) \quad (54)$$

Substituting $\text{const} = P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ into (54)

$$W_{12} = \frac{1}{1-\gamma}(P_2 V_2 - P_1 V_1) \quad (55)$$

Using (5) and (50) one can simplify this formula to

$$W_{12} = \frac{nR}{1-\gamma}(T_2 - T_1) = C_V(T_1 - T_2) \quad (56)$$

## ALTERNATIVELY...

According to first law of thermodynamics
in adiabatic process work is equal to change of internal energy

$$W_{12} = U_1 - U_2$$

For ideal gas ☛ $U = U(T)$ and $dU/dT = C_V$

Internal energy of ideal gas is given by $U(T) = \int C_V\,(T)\,dT$ (57)

For perfect gas ☛ $C_V = \text{const}$

$$U(T) = C_V\,T + U_0 \qquad U_0 = \text{const} \qquad (58)$$

$$U_1 - U_2 = C_V(T_1 - T_2) \qquad (59)$$

so that (56) follows

# HEAT MACHINES

Heat machines were a major application of thermodynamics in XIX century

Basis of their understanding is first law of thermodynamics (25)

Heat machine includes two reservoirs with different temperatures and a system that exchanges heat with two reservoirs and does work in a cyclic process

There are three types of heat machines:

**engines, refrigerators and heat pumps**

Engines of XIX century used steam as a source of heat

⬇

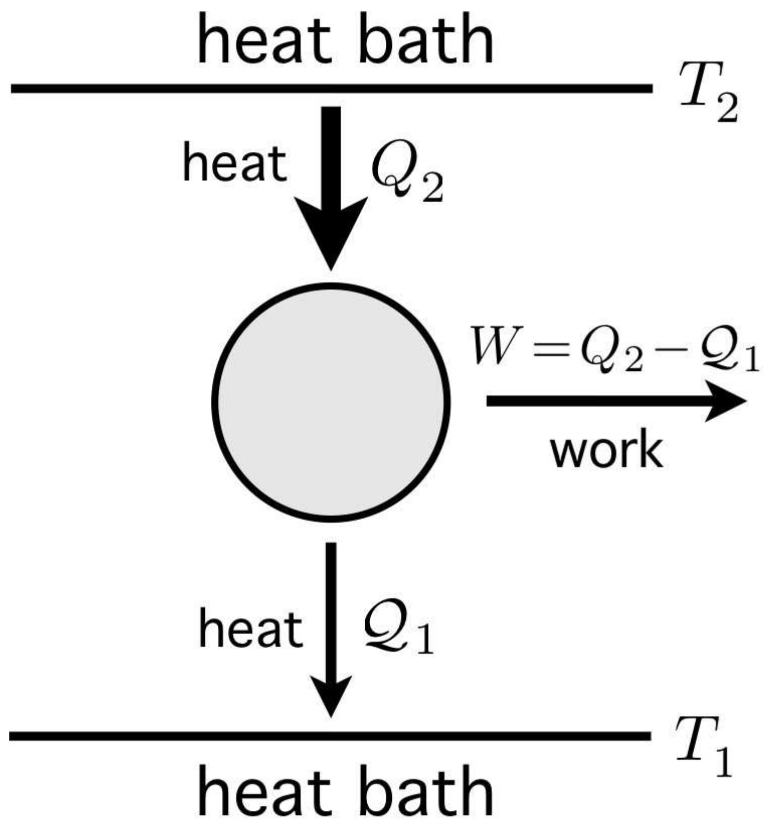
(obtained by heating water by fire)

Contemporary motors use fuel that burns and generates heat directly

Refrigerators and heat pumps also use agents other than water

# HEAT ENGINE

During one cycle system receives heat $Q_2$ from hot reservoir
gives heat $Q_1$ to cold reservoir and makes work $W$



# EFFICIENCY OF HEAT ENGINE

Efficiency of engine ☛ ratio of output energy to input energy

$$\eta = \frac{W}{Q_2} \qquad (\mathcal{Q}_1 \text{ is lost energy}) \qquad (60)$$

In cyclic processes internal energy of system does not change:

$$\Delta U = \oint dU = 0 \qquad (61)$$

Integrating (25) over cycle

$$0 = \oint (\delta Q - \delta W) = Q - W = Q_2 - \mathcal{Q}_1 - W \qquad (62)$$

so that the work done by the system is $W = Q_2 - \mathcal{Q}_1$

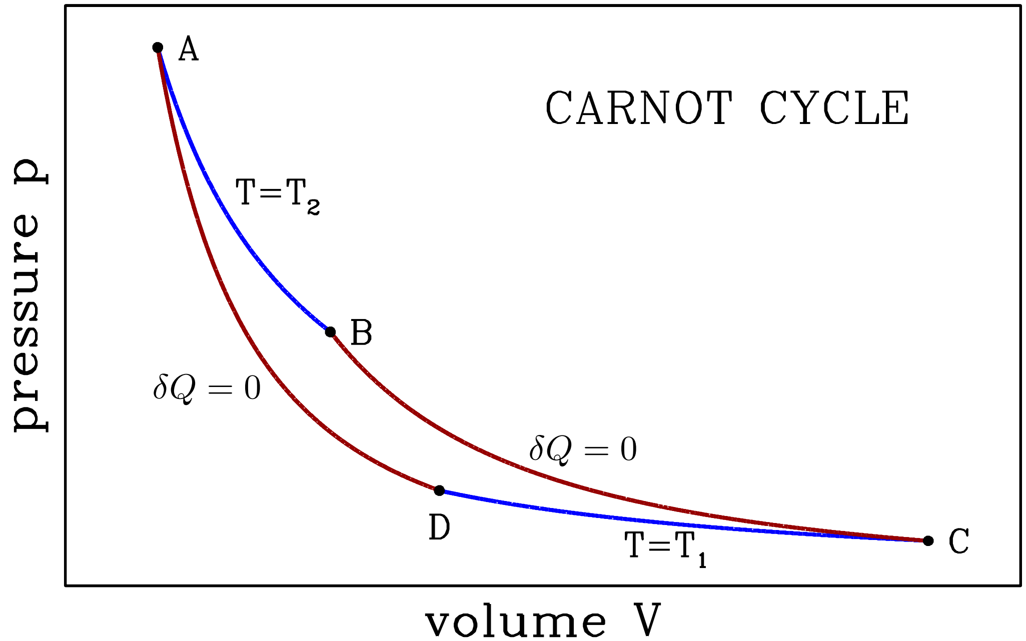
Inserting this into (60) ☛ $\eta = 1 - \frac{\mathcal{Q}_1}{Q_2}$ (63)

Note that $\eta < 1$

To make efficiency $\eta$ as high as possible we should minimize $\mathcal{Q}_1$

# CARNOT CYCLE

Carnot cycle consists of two isotherms $T_1$ and $T_2$ and two adiabats (working body being ideal gas)




Cycle goes clockwise ☛ work done by system $W = \oint P dV > 0$

Heat $Q_2$ is received on the isothermal path $AB$ at $T = T_2$

Heat $Q_1$ is given away on isothermal path $CD$ at $T = T_1$

There is no heat exchange on the adiabatic paths $BC$ and $DA$

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# CARNOT ENGINE

For ideal gas $U = U(T)$ ☛ along isotherms $U = \text{const}$

$$dU = \delta Q - \delta W = 0$$

Using (20):

$$Q_2 = Q_{AB} = W_{AB} = nRT_2 \ln \frac{V_B}{V_A}$$
$$\mathcal{Q}_1 = -Q_{CD} = -W_{CD} = nRT_2 \ln \frac{V_C}{V_D} > 0 \quad (64)$$

Using (51):

$$T_2 V_B^{\gamma-1} = T_1 V_C^{\gamma-1} \qquad T_2 V_A^{\gamma-1} = T_1 V_D^{\gamma-1} \quad (65)$$

Dividing these equations by each other ☛ $V_B/V_A = V_C/V_D$

$$\frac{\mathcal{Q}_1}{Q_2} = \frac{T_1}{T_2} \quad (66)$$

(63) gives Carnot formula for temperature scale

$$\eta = 1 - \frac{T_1}{T_2} \quad (67)$$

# EFFICIENCY OF CARNOT ENGINE

Efficiency $\eta$ becomes close to 1 as $T_1 \to 0$

practically it is impossible to realize

In standard engines $T_1$ is temperature at normal conditions $T_1 = 300\,K$

$T_2$ of hot reservoir must essentially exceed $T_1$

e.g. for $T_2 = 600\,K$ ☛ $\eta = 0.5$

In practice ☛ processes in heat engines deviate from Carnot cycle

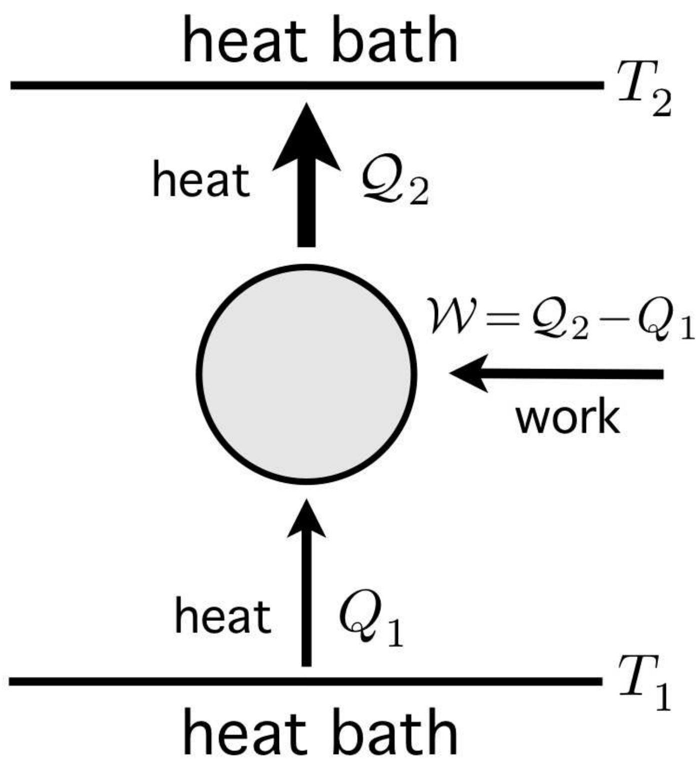
this leads to further decrease of efficiency $\eta$

# REFRIGERATOR

Refrigerators are inverted heat engines

Work is done on system that extracts heat $Q_1$ from cold reservoir (eventually lowering its temperature)

and gives heat $Q_2$ to hot reservoir ☛ the environment




(environment at $T_2$)

# EFFICIENCY OF REFRIGERATOR

Efficiency of refrigerator

$$c = \frac{\text{output}}{\text{input}} = \frac{Q_1}{\mathcal{W}} = \frac{Q_1}{\mathcal{Q}_2 - Q_1} \tag{68}$$

For Carnot refrigerator with help of (66)

$$c = \frac{T_1}{T_2 - T_1} \tag{69}$$

Efficiency of a refrigerator can be very high if $T_1$ and $T_2$ are close

This is the situation when the refrigerator starts to work

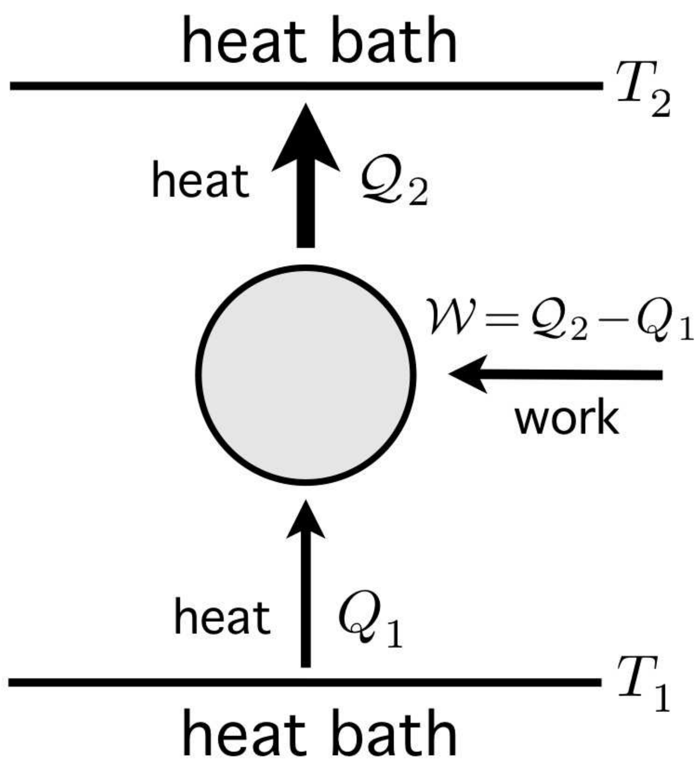
As $T_1$ decreases well below $T_2$ (environmental $300\,K$) efficiency becomes small

# HEAT PUMP

Similar to refrigerator but interpretation of reservoirs 1 and 2 changes

1 is the environment from where heat is being pumped

whereas 2 is the reservoir that is being heated (e.g. a house)




(environment at $T_1$ )

# EFFICIENCY OF HEAT PUMP

Efficiency

$$c = \frac{\text{output}}{\text{input}} = \frac{\mathcal{Q}_2}{\mathcal{W}} = \frac{\mathcal{Q}_2}{\mathcal{Q}_2 - Q_1} \qquad (70)$$

For Carnot heat pump efficiency becomes inverse of that of Carnot engine

$$d = \frac{T_2}{T_2 - T_1} \qquad (71)$$

Efficiency of heat pump is always greater than 1

If $T_1$ and $T_2$ are close to each other ☛ $d$ becomes large

This characterizes the initial stage of the work of a heat pump

After $T_2$ increases well above $T_1$ ☛ efficiency becomes close to 1

Heating a house in winter involves $T_1 \approx 270\,K$ while $T_2 \approx 300\,K$

☛ $d \approx 10$

In reality there are losses that lower heat pump efficiency

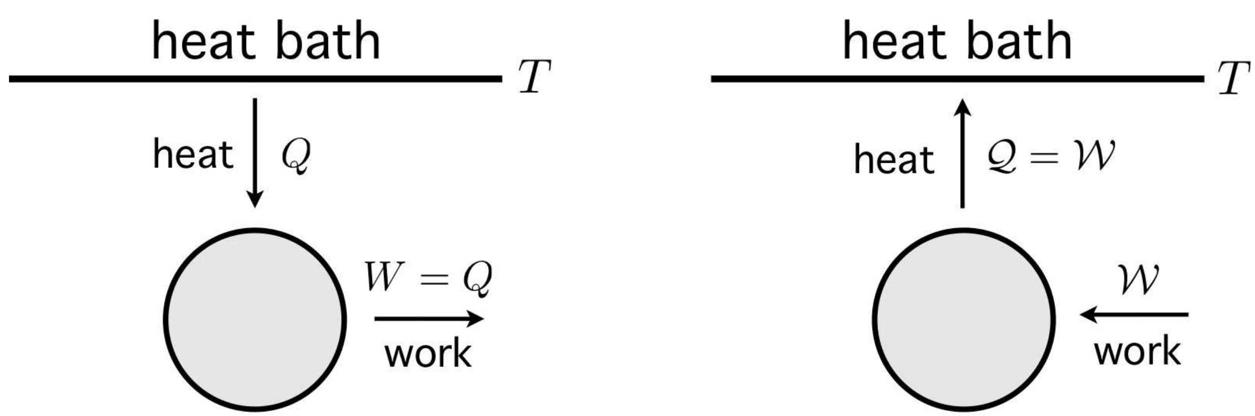
# THE SECOND LAW OF THERMODYNAMICS

**Postulate of Lord Kelvin:**

A transformation whose only final result is to extract heat from a source at fixed temperature and transform that heat into work is impossible

**Postulate of Clausius:**

A transformation whose only result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible




(a) a perfect engine (b) a perfect waste of time

These postulates which have been repeatedly validated by empirical observations constitute the Second Law of Thermodynamics

# CARNOT'S THEOREM

Efficiency of any reversible heat engine operating between heat reservoirs with temperatures $T_1$ and $T_2$ is equal to the efficiency of Carnot engine

$$\eta = 1 - T_1/T_2$$

while the efficiency of any irreversible heat engine is lower than this

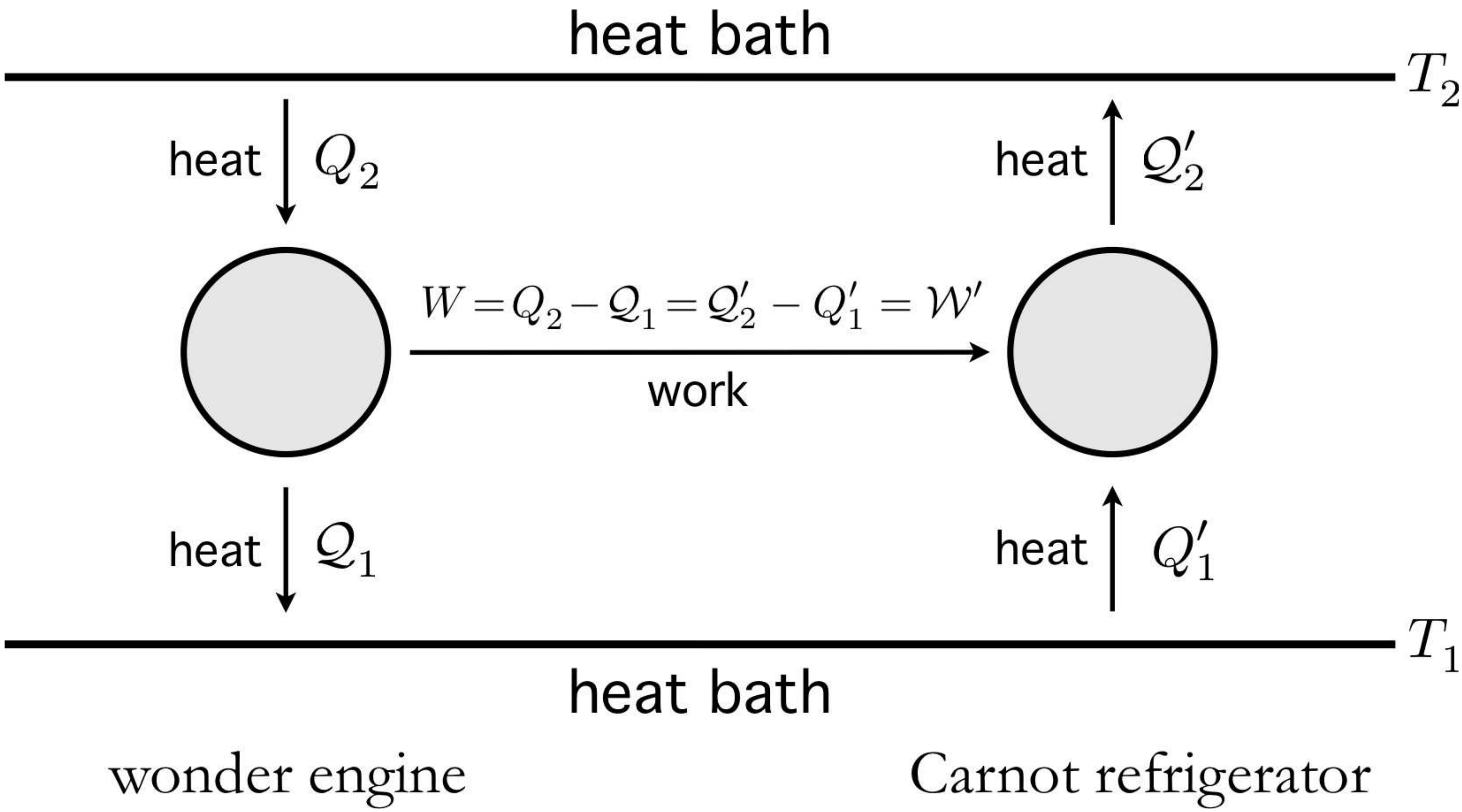
To prove Carnot's theorem ☛ assume that wicked awesome wonder engine has an efficiency greater than Carnot engine

Key feature of Carnot engine is its reversibility

we can go around its cycle in opposite direction ☛ creating a Carnot refrigerator

Envision wonder engine to driving a Carnot refrigerator

# WONDER ENGINE DRIVING CARNOT'S REFRIGERATOR



# NOTHING BEATS A CARNOT ENGINE

We assume
$$\frac{W}{Q_2} = \eta_{\rm wonder} > \eta_{\rm Carnot} = \frac{\mathcal{W}'}{\mathcal{Q}'_2} \qquad (72)$$

Looking @ figure
$$W = Q_2 - \mathcal{Q}_1 = \mathcal{Q}'_2 - Q'_1 = \mathcal{W}'$$

According to **second law of thermodynamics** ☛ $Q_2 - \mathcal{Q}'_2 \geq 0$ (73)

Difference of efficiencies

$$\eta - \eta' = \frac{W}{Q_2} - \frac{\mathcal{W}'}{\mathcal{Q}'_2} = \frac{W}{Q_2} - \frac{W}{\mathcal{Q}_2} = \frac{W(\mathcal{Q}'_2 - Q_2)}{Q_2 \mathcal{Q}'_2} \leq 0 \qquad (74)$$

that proves Carnot's theorem

In reversible case no heat flows from hot to cold reservoir and ☛ $\eta' = \eta$

# INFINITESIMALLY CARNOT CYCLE

Rewrite (74) using (63) for (arbitrary body) and (67) for (ideal gas)

$$\eta' - \eta = 1 + \frac{Q_1}{Q_2} - 1 + \frac{T_1}{T_2} = \frac{Q_1}{Q_2} + \frac{T_1}{T_2} \leq 0 \qquad (75)$$

Since $Q_2 > 0$ ☛

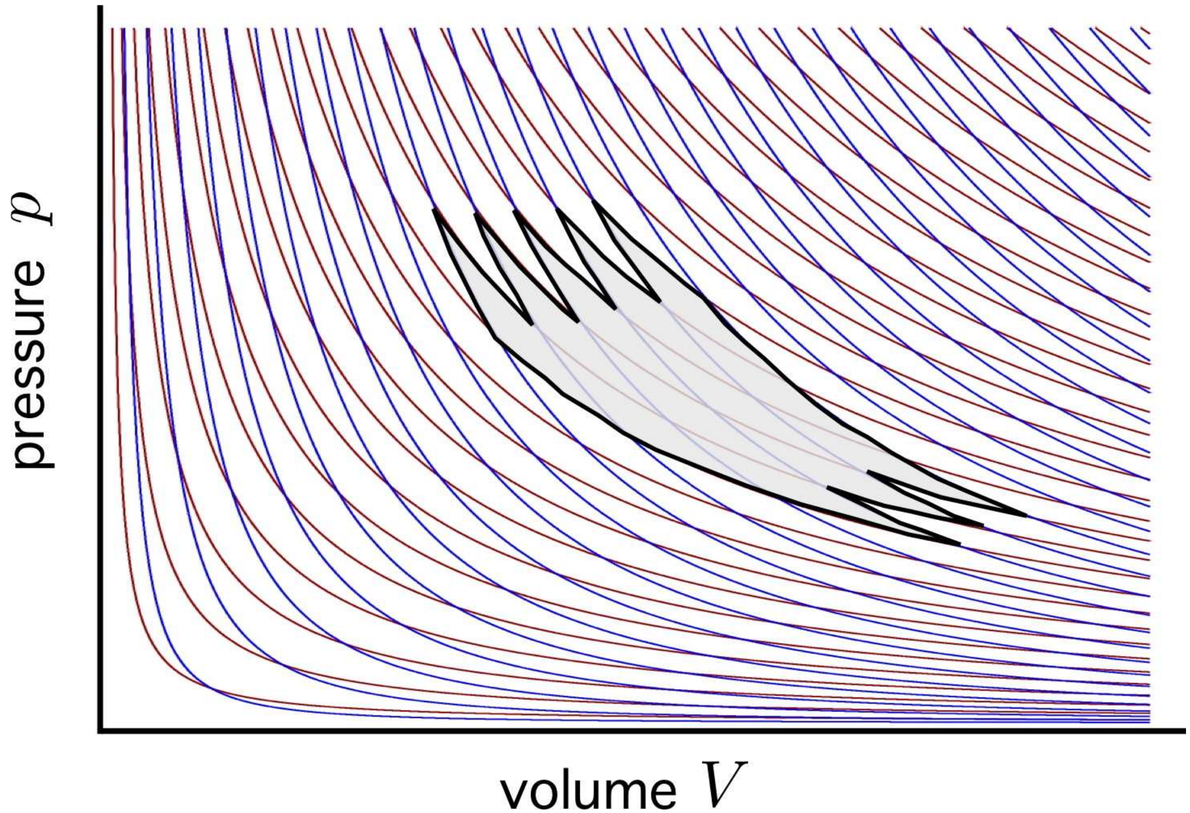
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0 \qquad (76)$$

For an infinitesimally narrow Carnot cycle

$$\frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} \leq 0 \qquad (77)$$

# CLAUSIUS INEQUALITY

Arbitrary curve in PV plane can be decomposed (to arbitrary accuracy) as combination of Carnot cycles




isotherms

adiabats

$$\gamma = \frac{5}{3}$$

Clausius inequality $$\oint \frac{\delta Q}{T} \leq 0 \quad (78)$$

with equality holding if all cycles are reversibles

# ENTROPY

Consequence of second law is existence of entropy:

a state function @ thermodynamic equilibrium whose differential is given by

$$\delta Q = T\, dS \tag{79}$$

$S$ being a state function ☛ does not change in any reversible cyclic process:

$$\oint \frac{\delta Q}{T} = 0$$

Since $Q$ is extensive ☛ so is $S$

Units of entropy are $[S] = \mathrm{J/K}$