Seminary on thermodynamics

Summary from course:

Perfect gas state equation:

$$\boxed{pV = nRT} \qquad R = 8310\ J/mol\,K$$

$$C_p = C_v + R \qquad \boxed{\gamma = \frac{C_p}{C_v}}$$ ratio of heat capacities

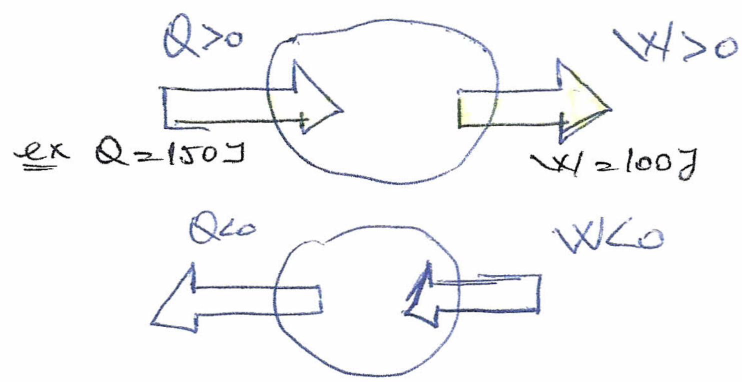
$$\begin{cases} C_p = \frac{5}{2}R \ ;\ C_v = \frac{3}{2}R & \text{monoatomic gas} \\ C_p = \frac{7}{2}R \ ;\ C_v = \frac{5}{2}R & \text{diatomic gas} \end{cases}$$

Laws of thermodynamics:

$\begin{cases} 0 \rightarrow \text{temperature} \\ +3 \text{ laws} \end{cases}$

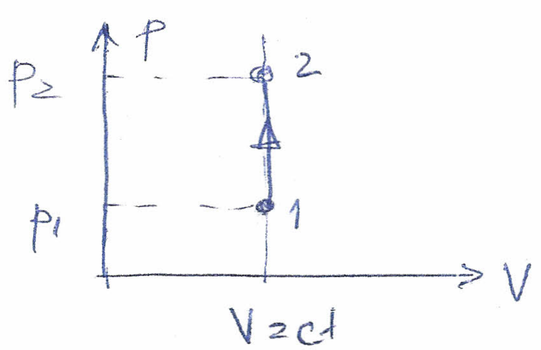
1. 1st law of thermodynamics:

$$\boxed{Q = \Delta U + W}$$



$\Delta U = Q - W = +50\ J$

Clapeyron representation p-V

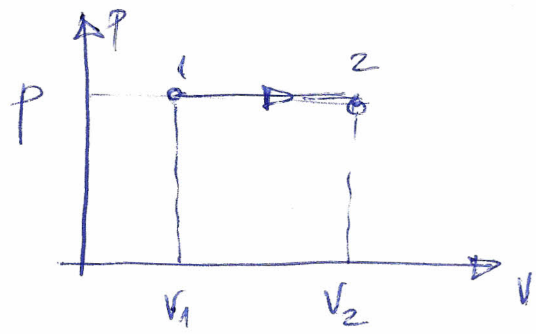


isochore transformation $V = ct$

$$W = \int_{V_1}^{V_2} p\,dV = 0$$

$$\Delta U = n C_v \Delta T = n C_v (T_2 - T_1)$$

$$Q = \Delta U = n C_v (T_2 - T_1)$$



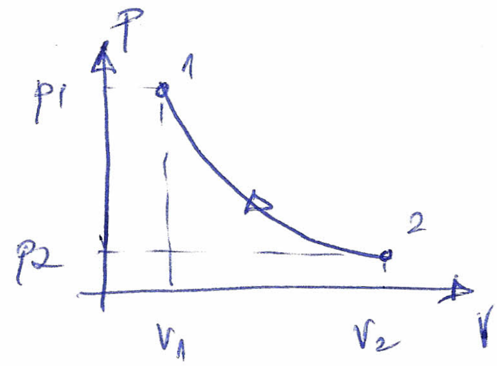
isobore transf. $\boxed{p = ct}$

$$W = p(V_2 - V_1) = nR(T_2 - T_1)$$

$$\Delta U = nC_v(T_2 - T_1)$$

$$Q = \Delta U + W = n(C_v + R)(T_2 - T_1)$$

$$Q = nC_p(T_2 - T_1)$$

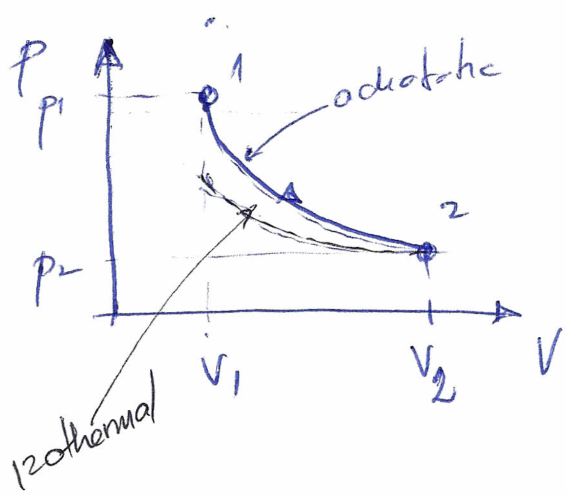


isotherme transf $\underline{T = ct}$

$$\Delta T = 0 \Rightarrow \Delta U = 0$$

$$Q = W = \int_1^2 p\,dV = \int_1^2 nRT \frac{dV}{V}$$

$$Q = W = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{p_1}{p_2}$$



transformation at $Q = ct$

$$Q = 0$$

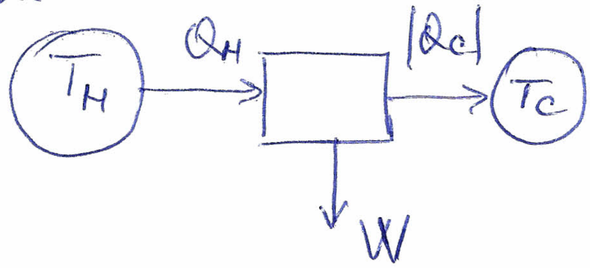
$$\Rightarrow \Delta U = -W$$

$$\begin{cases} \Delta U = nC_v(T_2 - T_1) = \frac{C_v}{R}(p_1V_1 - p_2V_2) \\ W = -nC_v(T_2 - T_1) \end{cases}$$

equation: $\begin{cases} pV^{\gamma} = ct \\ TV^{\gamma - 1} = ct \end{cases}$

② 2nd law of thermodynamics

engine



$W = Q_H - |Q_c|$

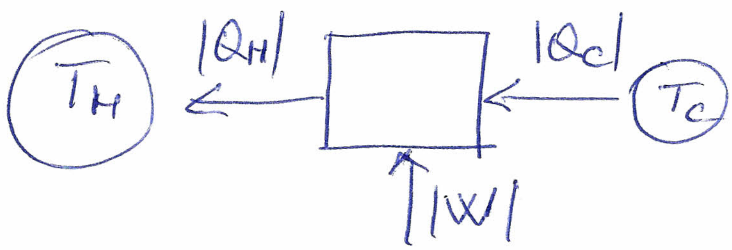
$$\boxed{e = \frac{W}{Q_H} = 1 - \frac{|Q_c|}{Q_H}}$$

efficiency.

→ allways two sources
hot T_H
cold T_c

→ heat transfer allways from hot to cold spontaneously (without external work).

with external work: ⇒ refrigerator



a work is done to force the heat transfer from cold (T_c) to hot (T_H)

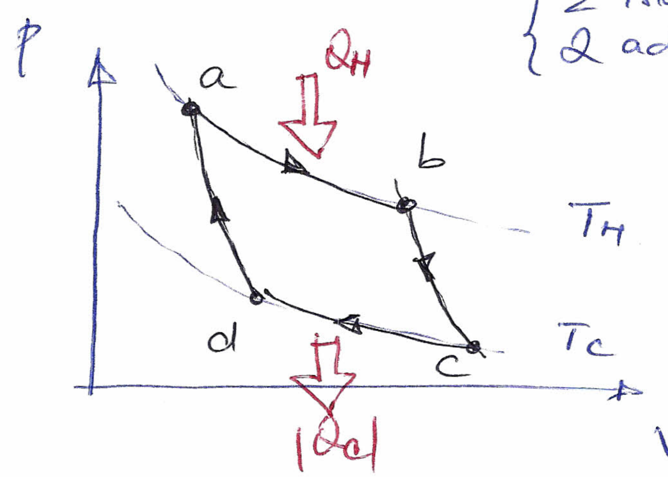
→ entropy ⇒ degree of disorder
In a spontaneous process $\Delta S > 0$. (allways)

$$dS = \frac{dQ}{T}$$

The Carnot cycle

According to the 2nd law, no engine can have 100% efficiency. How great would be the maximum efficiency of an engine operating between a hot source T_H and a cold source T_C. This question has been answered in 1826 by the French engineer Sadi Carnot who developed a theoretical idealized engine. The cycle of this engine is called the Carnot cycle. Let's calculate the efficiency of this engine.

In p-V representation: Carnot cycle composed by:
- 2 isothermes
- 2 adiabates



a→b: the gas expands isothermally at T_H absorbing heat Q_H

b-c adiabatic expansion ($Q=0$) until temperature decreases to T_C

c-d isothermal compression rejecting heat $|Q_C|$

d-a adiabatic compression to initial state at temperature T_H

Solution

$$e = 1 - \frac{|Q_C|}{Q_H}$$

$$Q_H = nRT_H \ln \frac{V_b}{V_a}$$

$$Q_C = nRT_C \ln \frac{V_d}{V_c} = -nRT_C \ln \frac{V_c}{V_d}$$

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H} \frac{\ln\left(\frac{V_c}{V_d}\right)}{\ln\left(\frac{V_b}{V_a}\right)}$$

This can be simplified by using T-V relationship for an adiabatic process $TV^{\gamma-1} = ct$

(1) $T_H V_b^{\gamma-1} = T_c V_c^{\gamma-1}$

(2) $T_H V_a^{\gamma-1} = T_c V_d^{\gamma-1}$

we divide (1) by (2)

$$\Rightarrow \left(\frac{V_b}{V_a}\right)^{\gamma-1} = \left(\frac{V_c}{V_d}\right)^{\gamma-1} \Rightarrow$$

$$\frac{V_b}{V_a} = \frac{V_c}{V_d}$$

$$\Rightarrow \frac{Q_c}{Q_H} = -\frac{T_c}{T_H}$$

or $$\frac{|Q_c|}{Q_H} = \frac{T_c}{T_H}$$

$$\Rightarrow \boxed{e_{Carnot} = 1 - \frac{T_c}{T_H}}$$

The efficiency of a Carnot engine depends only on the temperature of the heat reservoirs.

Caution

In all calculations involving the Carnot cycle you have to use ABSOLUTE TEMPERATURES ONLY.

Example

A Carnot engine takes 2000J of heat from a reservoir at 500 K, does some work and discards some heat to a reservoir at 350K. How much work does it do, how much heat is discarded and what is its efficiency?

Solution

$Q_H = 2000\,J$ $\qquad T_H = 500\,K$

$T_c = 350\,K$

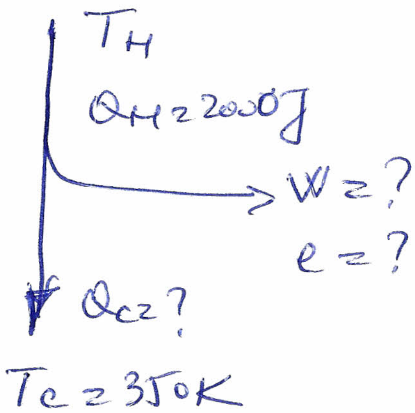
$$e = 1 - \frac{|Q_c|}{Q_H} = 1 - \frac{T_c}{T_H} \Rightarrow |Q_c| = Q_H \frac{T_c}{T_H}$$

$$\Rightarrow |Q_c| = 2000 \cdot \frac{350}{500} = 1400\,J$$

The work $\quad W = Q_H - |Q_c| = 2000 - 1400 = 600\,J$

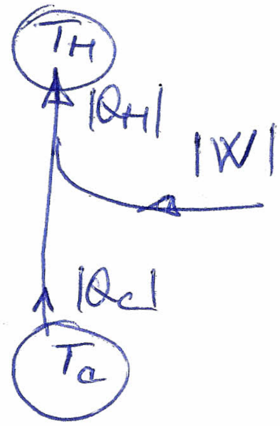
The efficiency: $\quad e = 1 - \frac{T_c}{T_H} = \frac{W}{Q_H} = \frac{600}{2000} = 0{,}3 = 30\%$

Sketch:

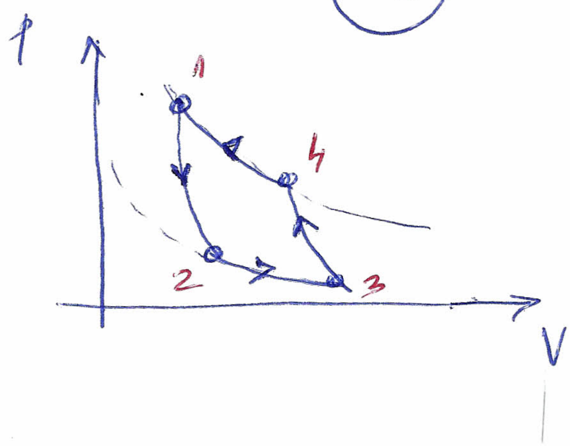


The Carnot refrigerator

If we reverse the Carnot engine cycle direction, we get a refrigerator. The coeff of performance:



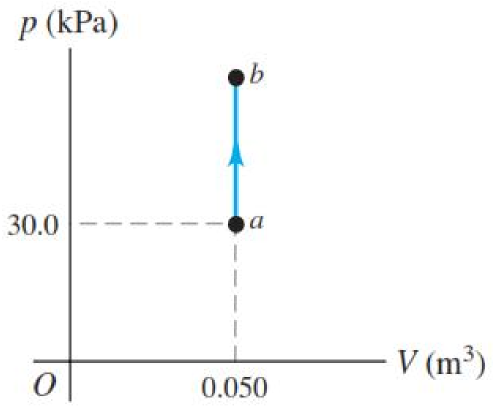
$$K = \frac{|Q_c|}{|Q_H| - |Q_c|} = \frac{|Q_c|}{W}$$



Solve again the 1st problem (Carnot cycle just inverted) and demonstrate that

$$\boxed{K_{Carnot} = \frac{T_c}{T_H - T_c}}$$

1/ An ideal gas is taken from a to b on the pV-diagram shown in Fig. During this process, 700 J of heat is added and the pressure doubles. (a) How much work is done by or on the gas? Explain. (b) How does the temperature of the gas at a compare to its temperature at b? Be specific. (c) How does the internal energy of the gas at a compare to the internal energy at b? Again, be specific and explain.



IDENTIFY: Apply $\Delta U = Q - W$ to the gas.

SET UP: For the process, $\Delta V = 0$. $Q = +700$ J since heat goes into the gas.

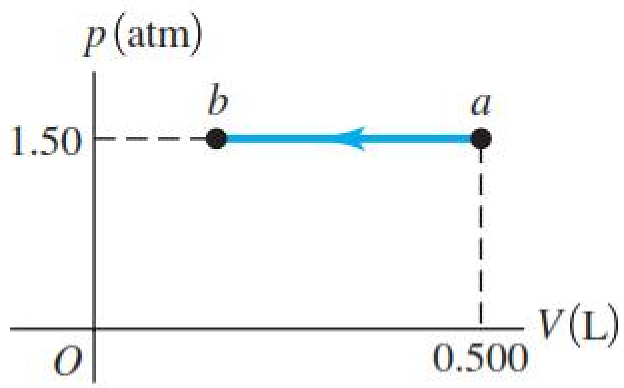
EXECUTE: **(a)** Since $\Delta V = 0$, $W = 0$.

(b) $pV = nRT$ says $\frac{p}{T} = \frac{nR}{V} =$ constant. Since p doubles, T doubles. $T_b = 2T_a$.

(c) Since $W = 0$, $\Delta U = Q = +700$ J. $U_b = U_a + 700$ J.

EVALUATE: For an ideal gas, when T increases, U increases.

2/ The Figure below shows a pV-diagram for an ideal gas in which its absolute temperature at b is one-fourth of its absolute temperature at a. (a) What volume does this gas occupy at point b? (b) How many joules of work was done by or on the gas in this process? Was it done by or on the gas? (c) Did the internal energy of the gas increase or decrease from a to b? How do you know? (d) Did heat enter or leave the gas from a to b? How do you know?



IDENTIFY: The gas is undergoing an isobaric compression, so its temperature and internal energy must be decreasing.

SET UP: The pV diagram shows that in the process the volume decreases while the pressure is constant. $1\text{ L} = 10^{-3}\text{ m}^3$ and $1\text{ atm} = 1.013 \times 10^5\text{ Pa}$.

EXECUTE: **(a)** $pV = nRT$. n, R and p are constant so $\frac{V}{T} = \frac{nR}{p} = \text{constant}$. $\frac{V_a}{T_a} = \frac{V_b}{T_b}$.

$$V_b = V_a\left(\frac{T_b}{T_a}\right) = (0.500\text{ L})\left(\frac{T_a/4}{T_a}\right) = 0.125\text{ L}.$$

(b) For a constant pressure process, $W = p\,\Delta V = (1.50\text{ atm})(0.125\text{ L} - 0.500\text{ L})$ and

$$W = (-0.5625\text{ L}\cdot\text{atm})\left(\frac{10^{-3}\text{ m}^3}{1\text{ L}}\right)\left(\frac{1.013\times10^5\text{ Pa}}{1\text{ atm}}\right) = -57.0\text{ J}.$$ W is negative since the volume decreases.

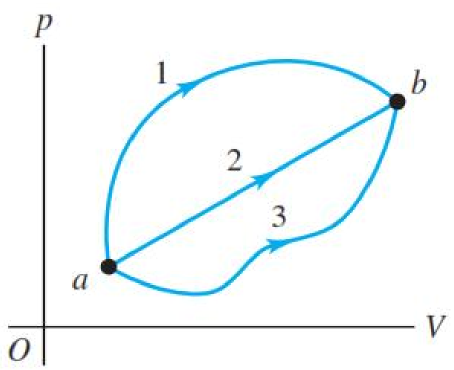
Since W is negative, work is done on the gas.

(c) For an ideal gas, $U = nCT$ so U decreases when T decreases. The internal energy of the gas decreases because the temperature decreases.

(d) For a constant pressure process, $Q = nC_p\,\Delta T$. T decreases so ΔT is negative and Q is therefore negative. Negative Q means heat leaves the gas.

EVALUATE: $W = nR\,\Delta T$ and $Q = nC_p\Delta T$. $C_p > R$, so more energy leaves as heat than is added by work done on the gas, and the internal energy of the gas decreases.

3/ A system is taken from state *a* to state *b* along the three paths shown in Fig below. (a) Along which path is the work done by the system the greatest? The least? (b) If Ub> Ua, along which path is the absolute value |Q| of the heat transfer the greatest? For this path, is heat absorbed or liberated by the system?



IDENTIFY: Apply $\Delta U = Q - W$. $|W|$ is the area under the path in the pV-plane.

SET UP: $W > 0$ when V increases.

EXECUTE: **(a)** The greatest work is done along the path that bounds the largest area above the V-axis in the p-V plane, which is path 1. The least work is done along path 3.

(b) $W > 0$ in all three cases; $Q = \Delta U + W$, so $Q > 0$ for all three, with the greatest Q for the greatest work, that along path 1. When $Q > 0$, heat is absorbed.

EVALUATE: ΔU is path independent and depends only on the initial and final states. W and Q are path dependent and can have different values for different paths between the same initial and final states.