

- ⇒ Any heat engine can have at most the efficiency of a Carnot engine
- All Carnot engines have the same efficiency

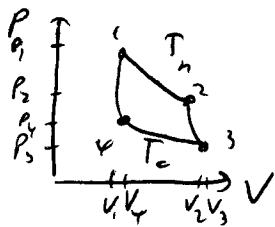
→ efficiency of Carnot engine depends on temperatures  $T_h$  and  $T_c$  only  
(independent of work substance, X, Y)

How does it depend on  $T_h$  and  $T_c$ ?

Use an example:

work substance: ideal gas  $PV = nRT$   $U = \frac{3}{2} nRT$

X: V  
Y: -P



isothermal change:

$$dU = \frac{3}{2} nR dT = 0$$

$$\Rightarrow dQ = dW = P dV = \frac{nRT_h}{V} dV$$

$$\Delta Q_h = nRT_h \int_{V_1}^{V_2} \frac{dV}{V} = nRT_h \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta Q_c = nRT_c \ln\left(\frac{V_3}{V_4}\right)$$

adiabatic change:

$$dQ = 0 = dU + P dV = \frac{3}{2} nR dT + P dV$$

$$\frac{3}{2} nR dT = -P dV = -\frac{nRT}{V} dV$$

$$\Rightarrow \frac{3}{2} \frac{dT}{T} = -\frac{dV}{V} \Rightarrow T^{3/2} V = \text{const.}$$

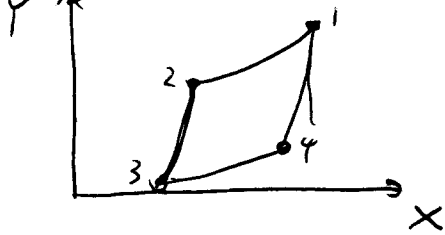
$$T_c V_3^{2/3} = T_h V_2^{2/3}$$

$$T_c V_4^{2/3} = T_h V_1^{2/3} \Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1}$$

$$\boxed{\eta = \frac{\Delta Q_h - \Delta Q_c}{\Delta Q_h} = 1 - \frac{T_c \ln(V_3/V_4)}{T_h \ln(V_2/V_1)} = 1 - \frac{T_c}{T_h}}$$

# Definition of entropy

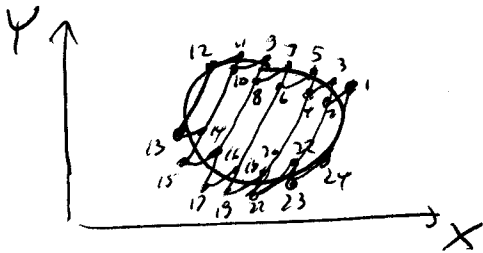
Carnot cycle



$$\frac{\Delta Q_{12}}{T_h} + \frac{\Delta Q_{34}}{T_c} = 0$$

$$\Delta Q_{23} = \Delta Q_{41} = 0$$

## Arbitrary reversible cycle:



an arbitrary cycle can be approximated by many Carnot cycles

$$\frac{\Delta Q_{12}}{T_{12}} + \frac{\Delta Q_{34}}{T_{34}} + \frac{\Delta Q_{56}}{T_{56}} + \dots = 0$$

$$\rightarrow \oint \frac{dQ}{T} = 0$$

$\Rightarrow \frac{dQ}{T}$  is an exact differential for reversible processes

$\Rightarrow$  defines state variable  $dS \equiv \frac{dQ}{T}$  "entropy"

## what about irreversible processes?

efficiency is smaller than Carnot efficiency

$$\rightarrow \oint \frac{dQ}{T} \leq 0 \quad (= \text{only if reversible})$$

$$\Rightarrow dS = \frac{dQ}{T} + d_i S \quad \text{with } d_i S \geq 0$$

if system is isolated:

$$dQ=0 \Rightarrow dS = d_i S \geq 0$$

in equilibrium  $dS=0$

"entropy always grows"  
"entropy is maximal"

Third Law

The difference in entropy between states connected by a reversible process goes to zero in the limit  $T \rightarrow 0K$

$$\Rightarrow \left(\frac{\partial S}{\partial Y}\right)_{N, T=0} = 0 \quad \left(\frac{\partial S}{\partial X}\right)_{N, T=0} = 0$$

" we can measure entropy in units such that  $S=0$  at  $T=0$ "

I.3 Fundamental equation of thermodynamics

reversible process:  $Tds = dU - YdX - \sum \mu_i^0 dN_i$  (\*)

$$S = S(U, X, N_1, \dots)$$

all the extensive variables:

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{X, \{N_i\}} = \frac{1}{T} \quad \text{thermal}$$

$$\left(\frac{\partial S}{\partial X}\right)_{U, \{N_i\}} = - \frac{Y}{T} \quad \text{mechanical}$$

$$\left(\frac{\partial S}{\partial N_i}\right)_{U, X, \{N_{i \neq j}\}} = - \frac{\mu_i^0}{T} \quad \text{chemical}$$

equation of state

extensivity of S:

$$\lambda S(U, X, \{N_i\}) = S(\lambda U, \lambda X, \{\lambda N_i\})$$



# I.4 Thermodynamic potentials

- A thermodynamic potential describes how much mechanical work can be maximally exerted by a thermodynamic system
- Thermodynamic potentials are minimized in thermodynamic equilibrium
- The knowledge of a thermodynamic potential as a function of its generic variables completely describes a system
- second derivatives of thermodynamic potentials give Maxwell relations
- first derivatives of thermodynamic potentials yield equations of state
- there is a <sup>thermodynamic</sup> potential for every (reasonable) set of variables / experimental setups

## I.4.1 Internal energy U

$$dU = dQ - dW = TdS - TdiS + YdX + \sum_0 \mu_i' dN_i$$

$$dU \leq TdS + YdX + \sum_0 \mu_i' dN_i$$

"=" if process are reversible

$$\Rightarrow U = U(S, X, \{N_i\})$$

EoS

~~$$\left(\frac{\partial U}{\partial S}\right)_{X, \{N_i\}} = T \quad \left(\frac{\partial U}{\partial X}\right)_{S, \{N_i\}} = Y \quad \left(\frac{\partial U}{\partial N_i}\right)_{S, X, \{N_{i \neq i}\}} = \mu_i'$$~~

For any change of the system at constant  $S, X, \{N_i\}$ .

$$\Delta U = \int dU \leq 0 \quad \text{with "=" for reversible changes}$$

Irreversible processes at constant  $S, X, \{N_i\}$  decrease the internal energy  $U$ . In thermodynamic equilibrium the internal energy  $U$  is minimized at fixed  $S, X, \{N_i\}$ .

for reversible changes  $dQ = T dS = 0$

for irreversible changes  $dQ = T dS - T d_i S < 0$

$\Rightarrow$  heat has to be expelled by the system in order to keep entropy constant  $\rightarrow$  if  $S$  more at  $dQ=0$

Ex. S.  $\left(\frac{\partial U}{\partial S}\right)_{X, \{N_i\}} = T$     $\left(\frac{\partial U}{\partial X}\right)_{S, \{N_i\}} = Y$    ,    $\left(\frac{\partial U}{\partial N_i}\right)_{S, X, \{N_{i \neq j}\}} = \mu_i'$

Maxwell relations

$$\left(\frac{\partial T}{\partial X}\right)_{S, \{N_i\}} = \left(\frac{\partial Y}{\partial S}\right)_{X, \{N_i\}} \quad \left(\frac{\partial T}{\partial N_i}\right)_{S, X, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_i'}{\partial S}\right)_{X, \{N_i\}}$$

$$\left(\frac{\partial Y}{\partial N_i}\right)_{S, X, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_i'}{\partial X}\right)_{S, \{N_i\}} \quad \left(\frac{\partial \mu_i'}{\partial N_i}\right)_{S, X, \{N_{i \neq j}\}} = \left(\frac{\partial \mu_i'}{\partial N_i}\right)_{S, X, \{N_{i \neq j}\}}$$

$\downarrow$  10/17