

# Heat and Work

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- Heat ( $Q$ ) and Work ( $W$ )
  - $Q$  is the energy transferred to  $S$  through thermal contact with  $R$
  - $W$  is work done by/on  $S$  through change in volume or external fields
- 1<sup>st</sup> Law of Thermodynamics

$$\delta Q = dU + \delta W$$

- $\delta$  is the inexact differential
- This means that:

$$\oint df = 0 \text{ or } \int_1^2 df = \int_1^2 df$$

\*  $df$  is independent of path

$$\oint \partial f \neq 0 \text{ and } \int_1^2 \partial f \text{ is path dependent}$$

- Note it *may* equal 0, but does not have to
- $U, \sigma$  are state functions, as they depend on state variables only ( $\tau, V, N, \dots$ )
  - $Q, W$  are not state functions (*i.e.* they are dependent on path)
- Let us consider a reversible process — a process that does not increase the total entropy of  $S + R$

$$\delta Q_{rev} = \tau d\sigma$$

- In general:

$$\delta Q \leq \tau d\sigma$$

- $Q$  is low quality energy; adding  $\delta Q$  to  $S$  increases its entropy by  $\delta Q/\tau$
- $W$  is high quality energy
- Heat engines convert heat to work
  - \* Steam engine
  - \* Internal combustion
  - \* Power plant
- Carnot efficiency  $\eta_c$ , is the ratio of work generated by  $S$  to heat added to  $S$  in a reversible process

$$\eta_c = \left( \frac{W}{Q_h} \right)_{rev}$$

- This can be rewritten in many forms, including:

$$\eta_c = \frac{Q_h - Q_l}{Q_h} = 1 - \frac{Q_l}{Q_h} = 1 - \frac{\tau_l}{\tau_h}$$

- The actual efficiency is:

$$\eta \leq \eta_c$$

- This can be obtained by assuming  $\sigma_h \leq \sigma_l$
- Refrigerators use work to move heat

- The Carnot efficiency for a refrigerator is:

$$\gamma_c = \left( \frac{Q_l}{W} \right)_{rev}$$

- This can be expressed in more useful terms for us as:

$$\gamma_c = \frac{\tau_l}{\tau_h - \tau_l}$$

- Similar to heat engines, we can say:

$$\gamma \leq \gamma_c$$

- Carnot Cycle

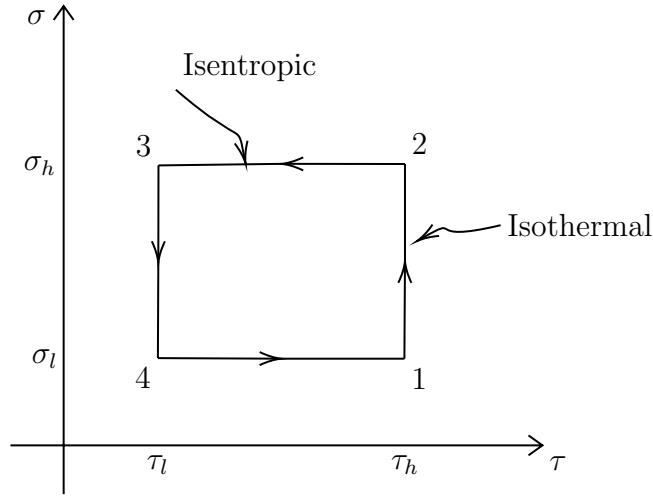


Figure 1: The Carnot Cycle

–  $1 \rightarrow 2$

- \*  $Q_{12} = \tau_h(\sigma_h - \sigma_l) > 0$

- \*  $W_{12} = \tau_h(\sigma_h - \sigma_l) - (U_2 - U_1)$

–  $2 \rightarrow 3$

- \*  $Q_{23} = 0$

- \*  $W_{23} = -(U_3 - U_2)$

–  $3 \rightarrow 4$

- \*  $Q_{34} = \tau_l(\sigma_l - \sigma_h) < 0$

- \*  $W_{34} = \tau_l(\sigma_l - \sigma_h) - (U_4 - U_3)$

–  $4 \rightarrow 1$

- \*  $Q_{41} = 0$

- \*  $W_{41} = -(U_1 - U_4)$

– Total

- \* Work:

$$(\tau_h - \tau_l)(\sigma_h - \sigma_l) > 0$$

- \* Heat:

$$(\tau_h - \tau_l)(\sigma_h - \sigma_l) > 0$$

– The efficiency may be defined as:

$$\eta = \frac{W_{tot}}{Q_{rec}} = 1 - \frac{\tau_l}{\tau_h}$$

- Subtle difference between isentropic and adiabatic (same if reversible): isentropic means constant entropy, adiabatic means no heat added to the system
- Carnot Cycle for an Ideal Gas (Spin 0, monatomic)

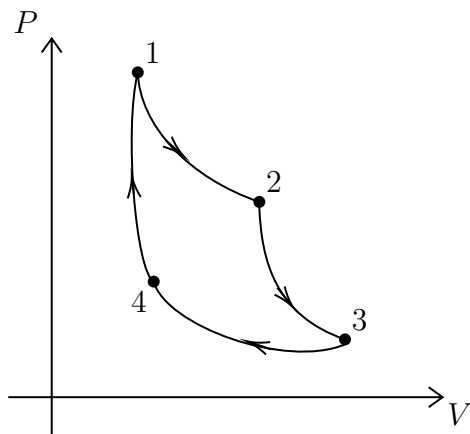


Figure 2:  $PV$  Diagram for Ideal Gas Carnot Cycle

- Process  $1 \rightarrow 2$  (Isothermal Expansion)
  - \*  $Q_{12} = \tau_h(\sigma_2 - \sigma_1) = \tau_h N \ln\left(\frac{V_2}{V_1}\right) > 0$
  - \*  $W_{12} = Q_{12}$  (from the  $\delta Q = dU + \delta W$ )
- Process  $2 \rightarrow 3$  (Isentropic/Adiabatic<sup>1</sup> Expansion)
  - \*  $Q_{23} = 0$
  - \*  $W_{23} = -\Delta U = -(U_3 - U_2) = \frac{3N}{2}(\tau_h - \tau_l) > 0$
- Process  $3 \rightarrow 4$  (Isothermal Contraction)
  - \*  $Q_{34} = \tau_l N \ln\left(\frac{V_4}{V_3}\right) = \tau_l N \ln\left(\frac{V_1}{V_2}\right) < 0$
  - \*  $W_{34} = Q_{34}$
- Process  $4 \rightarrow 1$  (Isentropic Contraction)
  - \*  $Q_{41} = 0$
  - \*  $W_{41} = -\Delta U = -(U_1 - U_4) - \frac{3N}{2}(\tau_l - \tau_h) < 0$

- Work done by a reversible process:

$$\delta W = \tau d\sigma - dU$$

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<sup>1</sup>Note; we may use either because the process is reversible

– Isothermal Process

$$\delta W = -d(U - \tau\sigma)$$

$$F = U - \tau\sigma$$

This gives us:

$$\delta W = -dF$$

$$W = -\Delta F$$

The work done by  $S$  in a reversible, isothermal process is  $-\Delta F$ ;  $W < -\Delta F$  if the process is irreversible. Thus, we can say the maximum work done by  $S$  in any process at constant temperature is  $\Delta F$ .

\* Isobaric Process

- \* The Work done by  $S$  on the environment is  $P dV$ , which is not very useful
- \* The effective work can be written:

$$\delta W' = \tau d\sigma - dU - P dV$$

- Under constant temperature:

$$\delta W' = -d(U + PV - \tau\sigma)$$

- We can introduce another quantity,  $G$ , the Gibbs free energy, such that:

$$\delta W' = -dG$$

$$W' = -\Delta G$$

- Similar statements for the Gibbs free energy can be made:  $W_{eff} = -\Delta G$  for a reversible process, and  $W_{eff} < -\Delta G$  for an irreversible process
- The enthalpy is  $H = U + PV$
- Considering a case where  $\delta W' = 0$  (no effective work is done):

$$\delta Q = d(U + PV)$$

$$Q = \Delta H$$