

Chapter 15 Engines and Refrigerators

We've looked at the basic laws and various constraints.
We now apply this to cycles which do work +
exchange heat with the environment.

A. The Carnot Cycle

→ will use Serway notes. Chapter 20 + 22

Chapter 20 Heat and the 1st Law
of Thermodynamics

20.1 Heat and Thermal Energy

Definitions:

calorie: amt. of heat required to raise
 1 g of water from 14.5°C to 15.5°C

Calorie = 1000 calories = 1 kcal.
 ↑ capital "C". (appears in the food industry)

BTU = British Thermal Unit = amt. of heat
 required to raise 1 lb of water from 63°F to 64°F

Joule = SI unit.

$$1 \text{ kcal} = 4.186 \text{ J.}$$

Example: Losing Weight the Hard Way

Burning off a large meal by exercise.

$$\begin{aligned} 1 \text{ large meal} &\approx 2000 \text{ Calories} = 2 \times 10^6 \text{ calories} \\ &= 2 \times 10^6 \times 4.186 \text{ J/cal} = 8.37 \times 10^6 \text{ J.} \end{aligned}$$

Lifting $50 \text{ kg} \times 2 \text{ m.} \times n$ times to use $8.37 \times 10^6 \text{ J}$

implies:

$$n = \frac{8.37 \times 10^6}{\underbrace{50 \times 2 \times 9.8 \text{ m/s}^2}_{mgh}} = \underline{\underline{8.54 \times 10^3 \text{ times!}}}$$

20.2 Heat Capacity and Specific Heat

When heat, Q , is added to a mass, m , the temperature rise is governed by

$$Q = m c \Delta T$$

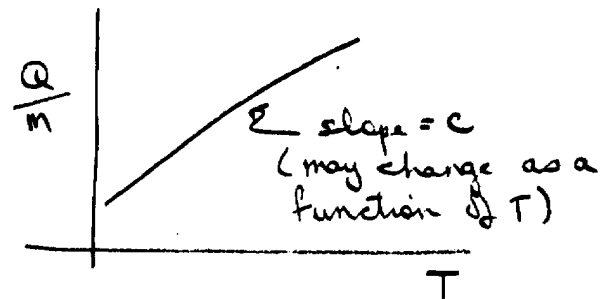
where c = heat capacity, $J/kg^\circ C$

if no work is done and no phase change occurs.

More precisely:

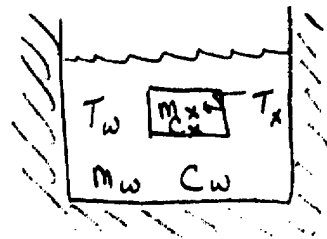
$$Q = m \int_{T_1}^{T_2} c(T) dT$$

$$\text{or } \frac{dQ}{dT} = m c(T)$$



Calorimetry

If we mix a known quantity, m_x of a substance, whose c we don't know, with a substance whose m & c are known (say water), then we can find c_x by measuring T 's before and after mixing



$$\underbrace{m_w c_w (T - T_w)}_{\text{energy gained by water}} = \underbrace{-m_x c_x (T - T_x)}_{\text{energy lost by x}}$$

energy gained by water = energy lost by x

$$\therefore c_x = \frac{m_w c_w (T - T_w)}{m_x (T_x - T)}$$

Example: Cooling a Hot Ingot

$$M_x = 0.05 \text{ kg}$$

$$M_w = 0.4 \text{ kg}$$

$$T = 224^\circ\text{C}$$

$$T_x = 200^\circ\text{C}$$

$$T_w = 20^\circ\text{C}$$

Find C_x .

$$C_x = \frac{0.4 \text{ kg} \times 4186 \text{ J/kg}^\circ\text{C} (22.4 - 20)}{0.05 \text{ kg} \times (200 - 22.4)}$$

$$= 453 \text{ J/kg}^\circ\text{C} \leftarrow \text{This is close to } C \text{ for iron.}$$

20.3 Latent Heat

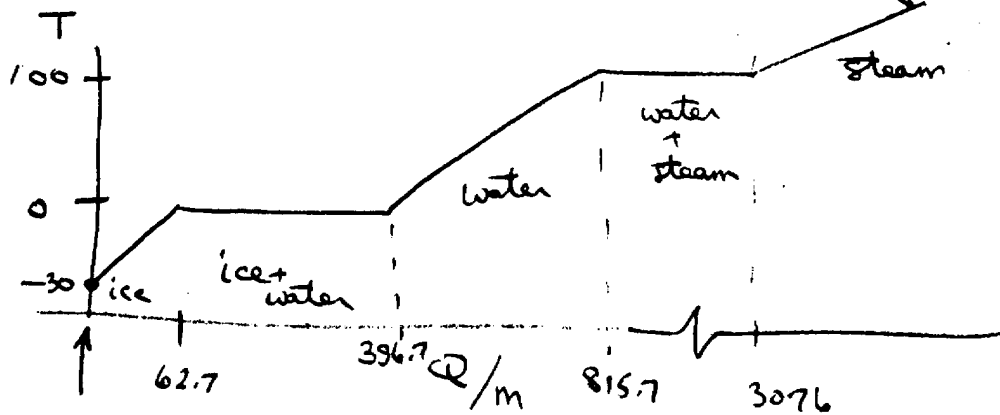
During a phase change:

$$Q = m L$$

↑ latent heat (J/kg)

L_f = latent heat of fusion (solid to liquid)

L_v = " " " " vaporization (liquid to vapour)

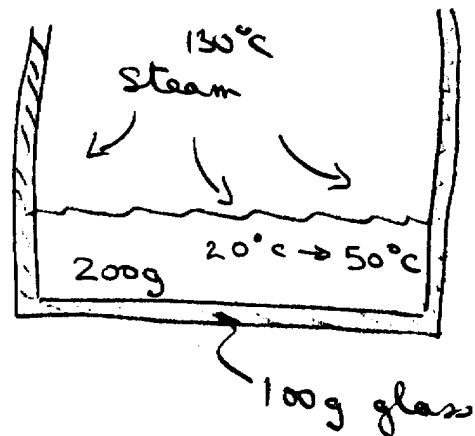


arbitrary
reference point.

$$\frac{Q}{m} = c_i \Delta T_{ice} + L_f + c_w \Delta T_w + L_v + c_s \Delta T_s$$

Example: Cooling the steam

What mass of steam is needed to warm the water and glass from $20^\circ\text{C} \rightarrow 50^\circ\text{C}$?



$$Q = \underbrace{m_s c_s \Delta T}_{\substack{\text{steam} \\ 130^\circ\text{C} \rightarrow 100^\circ\text{C}}} + \underbrace{m_s L_v}_{\substack{\text{steam} \\ \text{condensation}}} + \underbrace{m_s c_w \Delta T}_{\substack{\text{water} \\ 100^\circ\text{C} \rightarrow 50^\circ\text{C}}}$$

$$= \underbrace{m_w c_w \Delta T}_{\substack{\text{water warming} \\ 20^\circ\text{C} \rightarrow 50^\circ\text{C}}} + \underbrace{m_g c_g \Delta T}_{\substack{\text{glass warming} \\ 20^\circ\text{C} \rightarrow 50^\circ\text{C}}}$$

$$\therefore m_s \left[(2.01 \times 10^3 \text{ J/kg}^\circ\text{C})(30^\circ\text{C}) + 2.26 \times 10^6 \text{ J/kg} + 4.19 \times 10^3 \text{ J/kg}^\circ\text{C} \times 50^\circ\text{C} \right]$$

$$= 0.2 \times 4.19 \times 10^3 \text{ J/kg}^\circ\text{C} \times 30^\circ\text{C} + 0.1 \times 837 \text{ J/kg}^\circ\text{C} \times 30^\circ\text{C}$$

$$\therefore m_s = 10.9 \times 10^{-3} \text{ kg} = \underline{\underline{10.9 \text{ g}}}$$

20.4 Work and Heat in Thermodynamic Processes

State variables:

microscopic $e, T, P, e \dots$

any 2 fully describes a homogeneous substance in equilibrium.

macroscopic $M, V, T, P, e \dots$

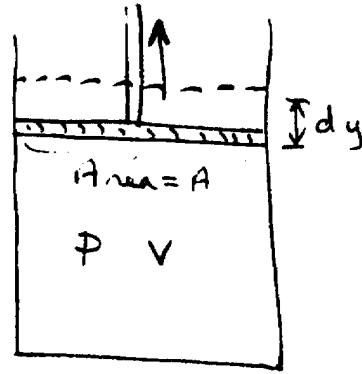
any 3 fully describes a homogeneous substance in equilibrium.

We consider a gas in thermodynamic equilibrium next.

Expand the gas quasi-statically, i.e. slowly so gas remains in equilibrium:

$$dW = F dy = PA dy = PdV$$

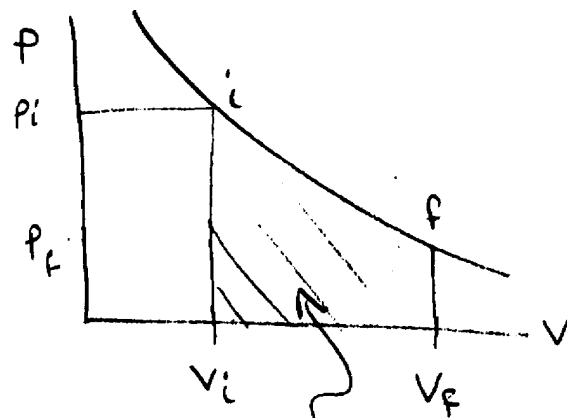
= work done by the gas on the piston.



$$\underline{\underline{dW = PdV}}$$

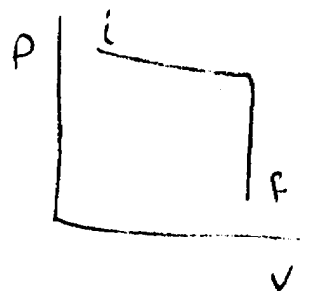
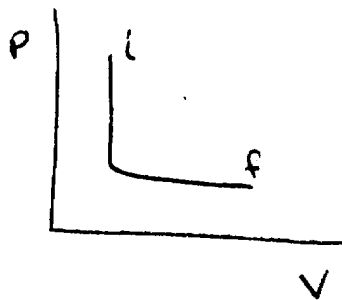
$$\therefore W = \int_{V_i}^{V_f} PdV$$

= area under curve on a PV diagram.



Note

The work done depends on the path.



↗ same initial & final states but the work done is very different.

20.5 The First Law of Thermodynamics

$$\Delta U = U_f - U_i = Q - W$$

or

$$dU = dQ - dW$$

\uparrow energy transferred to system \uparrow work done by the system

- U is a state function (i.e. internal energy is a condition of the state of a substance - independent of how it got there, i.e. independent of the path)
- $Q + W$ both depend on the path but $Q - W$ doesn't!
- In an isolated system, $Q = W = 0 \therefore \Delta U = 0$.
- In a non-isolated system that cycles (i.e. final state = initial state)

$$\Delta U = 0 \Rightarrow Q = W$$

Note that the area enclosed by the cycle on a PV diagram = net work done per cycle.

20.6 Some Applications of the First Law of Thermodynamics

Adiabatic Process: $Q = 0$, ie no thermal energy enters or leaves the system.

$$\therefore \Delta U = -W$$

Thus if a gas expands adiabatically, the system does work on its surroundings $\Rightarrow W > 0$.
 $\Rightarrow \Delta U < 0 \therefore T_{\text{gas}} \downarrow$. The converse is true.

Examples:

- expansion of hot gases in the internal combustion engine.
- liquefaction of gases in a cooling system
- compression stroke in a diesel engine.

Adiabatic Free Expansion: $Q = 0$
 $W = 0$ (no work done)

$\therefore \Delta U = 0 \therefore$ no change in temperature.

Isobaric Process : $P = \text{constant}$

$$W = P(V_f - V_i)$$

$$Q = 0 \text{ (usually)} \Rightarrow \Delta U = -W$$

Isochoric Process : $V = \text{constant}$

Since $V = \text{constant}$, $W = 0$

$$\therefore \Delta U = Q$$

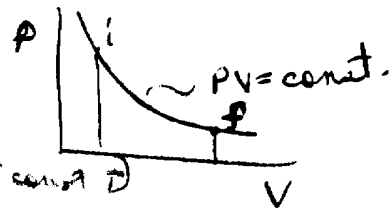
Example: Combustion in a gasoline engine occurs quickly. All the Q is added before any ΔV occurs. $\therefore \Delta U \uparrow \therefore T \uparrow$

Isothermal Process : $T = \text{constant}$

For an ideal gas, $PV = nRT$

$\therefore PV = \text{constant} \Rightarrow$

$$\Rightarrow \Delta U = 0 \quad \left(\begin{array}{l} E = \frac{1}{2} kVNT \\ = \text{const at const } T \end{array} \right)$$



Since work is done by the system, some Q must be added to maintain T constant.

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln V \Big|_{V_i}^{V_f}$$

state $P, T = 0$

$$= nRT \ln(V_f/V_i)$$

$$= Q \text{ added.}$$

$$\therefore \Delta E = \Delta Q - W + \mu \Delta N$$

$$= 0$$

ideal gas
 $PV = nRT$
 $\therefore \frac{\partial P}{\partial T} = \frac{nR}{V}$

$$\therefore dQ = T \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\therefore Q = T \int_{V_i}^{V_f} \frac{nR}{V} dV = nRT \ln V_f/V_i$$

Example: Work Done During an Isothermal Expansion

1 mole of an ideal gas at 0°C , $V_i = 3\text{ l}$, $V_f = 10\text{ l}$.

Find W .

$$\begin{aligned} W &= nRT \ln(V_f/V_i) \\ &= 1 \text{ mol} \times 8.31 \text{ J/mol}\cdot\text{K} \times 273 \text{ K} \times \ln(10/3) \\ &= 2.7 \times 10^3 \text{ J} = Q_{\text{added}}. \end{aligned}$$

Boiling

Consider vaporizing m kg of liquid at constant pressure.

$$W = \int_{V_l}^{V_v} P \cdot dV = P \int dV = P(V_v - V_l)$$

$v = \text{vapour}$
 $l = \text{liquid}$

$$Q_{\text{added}} = mL_v$$

$$\therefore \Delta U = Q - W = mL_v - P(V_v - V_l)$$

Example: Boiling Water

1 gm at $P = P_{\text{atm}}$, $V_l = 1 \text{ cm}^3$. Find ΔU .

$$Q = mL_v = (1.0 \times 10^{-3} \text{ kg}) \times (2.26 \times 10^6 \text{ J/kg}) = 2260 \text{ J}$$

$$\begin{aligned} W &= P(V_v - V_l) = (1.013 \times 10^5 \text{ N/m}^2) [1671 - 1.00] \times 10^{-6} \text{ m}^3 \\ &= 169 \text{ J} \end{aligned}$$

$$\therefore \Delta U = Q - W = 2260 \text{ J} - 169 \text{ J} = 2.09 \text{ kJ}$$

ie 93% of the heat added goes to ΔU , 7% goes to work.

Chapter 22 Heat Engines, Entropy and the Second Law of Thermodynamics

First law states that energy is conserved.

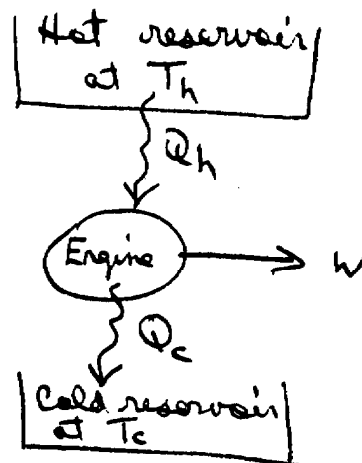
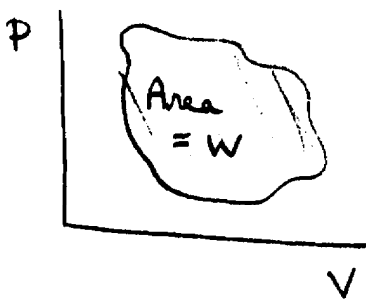
Second law establishes which processes can and cannot occur.

22.1 Heat Engines and the Second Law of Thermodynamics

Heat Engine:

- Working substance

- cyclic process $\Rightarrow \Delta U = 0 \Rightarrow W = Q_h - Q_c$



Thermal Efficiency, $e \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$

Typically, $e \sim 20 \rightarrow 40\%$ in engines.

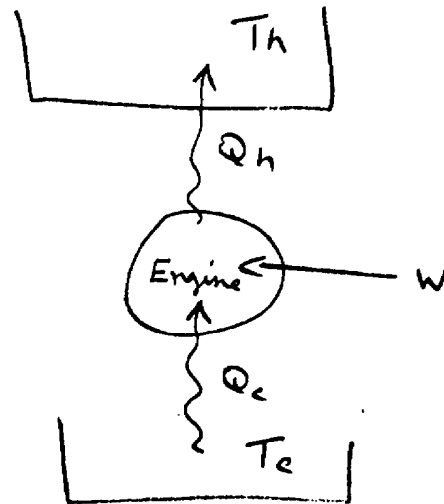
2nd Law: It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of thermal energy from a reservoir and the performance of an equal amount of work. (Kelvin-Planck)

- in short: $Q_c \neq 0$

Refrigerators and Heat Pumps

These are heat engines in reverse.

Must do work, W , to cause thermal energy to flow from cold reservoir to hot reservoir. (Clausius)

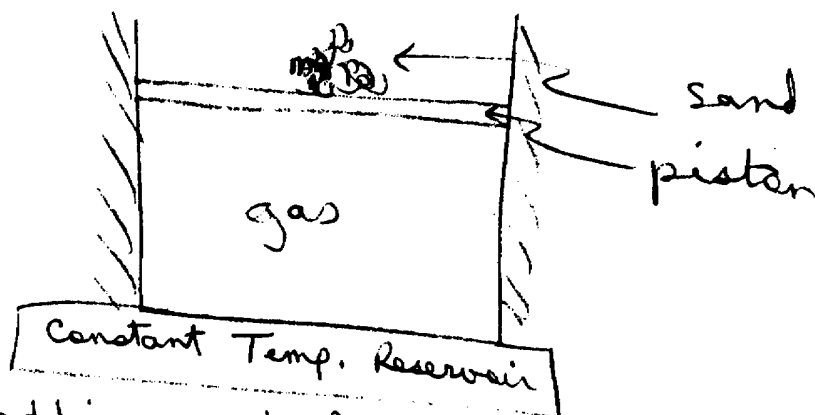


22.2 Reversible and Irreversible Processes

Reversible Process: one that can be performed so that, at its conclusion, both the system and its surroundings have been returned to their exact initial conditions.

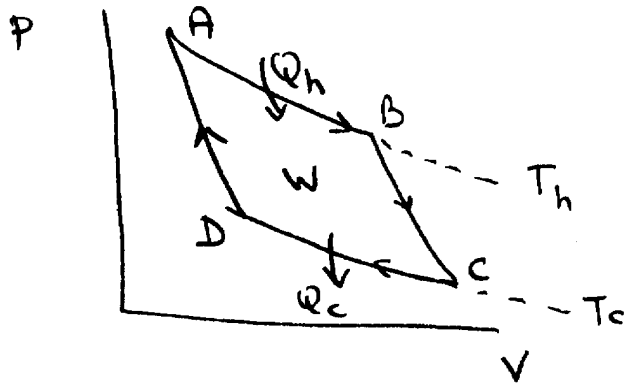
Irreversible Process: one that does not satisfy the above.

All real processes are irreversible but in some cases we can approximate a reversible process by minimizing dissipation effects such as friction.



slowly adding grains of sand causes a reversible compression of the gas - i.e. the system looks reversible but the surroundings are not.

22.3 The Carnot Engine

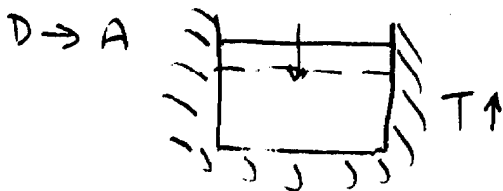
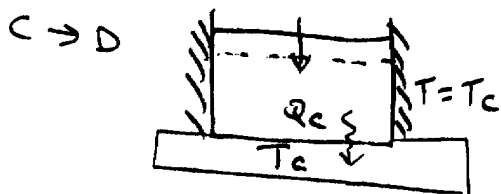
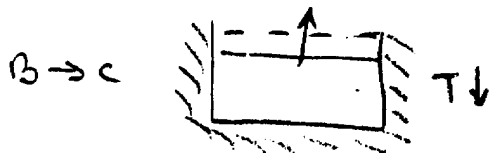
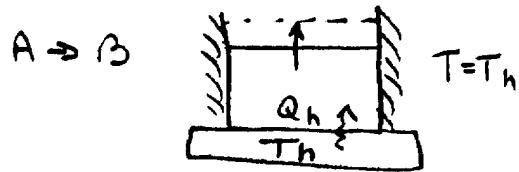


A \rightarrow B Isothermal expansion at T_h
 $Q = Q_h$ (= heat added)

B \rightarrow C Adiabatic expansion
 $Q = 0$

C \rightarrow D Isothermal compression at T_c
 $Q = Q_c$ (= heat rejected)

D \rightarrow A Adiabatic compression
 $Q = 0$



A → BT constant $\therefore \Delta U_{\text{gas}} = 0$

$$\therefore Q_h = W_{AB} = nRT_h \ln(V_B/V_A)$$

C → D

Similar to A → B

$$\therefore Q_c = -W_{CD} = nRT_c \ln(V_c/V_D)$$

B → C

Adiabatic, quasi-static expansion.

$$\therefore PV^\gamma = \text{constant}$$

$$\& PV = nRT$$

$$\Rightarrow TV^{\gamma-1} = \text{constant}$$

$$\therefore T_h V_B^{\gamma-1} = T_c V_c^{\gamma-1}$$

D → A

Similar to B → C

$$\therefore T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

$$\therefore \left(\frac{V_D}{V_A}\right)^{\gamma-1} = \left(\frac{V_c}{V_B}\right)^{\gamma-1} \Rightarrow \frac{V_B}{V_A} = \frac{V_c}{V_D}$$

$$\therefore \frac{Q_c}{Q_h} = \frac{nRT_c \ln(V_c/V_D)}{nRT_h \ln(V_B/V_A)} = \frac{T_c}{T_h}$$

$$\therefore e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h} \leftarrow \text{for Carnot Cycle}$$

from Serway Chapter 21:

$$du = nC_v dT = \underbrace{-P dV}_{-w}$$

but $PV = nRT$ if ideal gas

$$\therefore PdV + VdP = nRdT \leftarrow$$

$$\therefore PdV + VdP = -\frac{R}{C_v} PdV$$

$$\text{Now } R = C_p - C_v$$

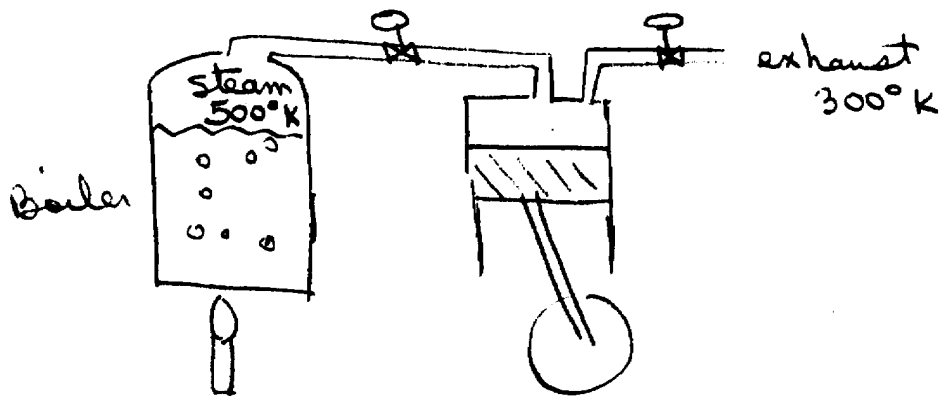
$$\therefore \frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

$$\text{where } \gamma = C_p/C_v$$

$$\Rightarrow \ln P + \gamma \ln V = \text{constant}$$

$$\therefore PV^\gamma = \text{constant.}$$

Example: The Steam Engine



Find maximum efficiency.

$$e_{\text{carnot}} = 1 - \frac{T_c}{T_h} = 1 - \frac{300\text{K}}{500\text{K}} = 0.4 \text{ or } \underline{40\%}$$

Find W_{max} if $Q_h = 200 \text{ J}$.

$$e = 1 - \frac{Q_c}{Q_h} = \frac{W}{Q_h} = 0.4 \quad \therefore \quad W = 0.4 \times 200 \text{ J} = \underline{80 \text{ J}}$$

Example: The Carnot Efficiency

Gas engine, $e = 30\%$, $T_c = 300\text{K}$, $T_h = ?$
(assume Carnot)

$$e = 0.3 = 1 - \frac{T_c}{T_h} \quad \therefore \quad T_h = \frac{T_c}{1-e} = \frac{300}{.7} = \underline{\underline{492 \text{ K}}}$$

If $Q_h = 837 \text{ J}$ find W .

$$W = e Q_h = 0.3 \times 837 \text{ J} = \underline{\underline{251 \text{ J}}}$$

22.4 The Absolute Temperature Scale

We can use the Carnot cycle as a means of measuring temperature.

Choose a reference temperature: 273.16 K
 (triple point of water, i.e. the temp. at which water in vapour, liquid and ice coexist -
 $T = 0.01^\circ\text{C}$, $P = 4.58 \text{ mm. Hg}$)

For Carnot cycle we showed that

$$\frac{T_c}{T_h} = \frac{Q_c}{Q_h}$$

- Run a substance through the Carnot cycle wherein $T_c = 273.16 \text{ K}$.
- Measure $Q_c + Q_h$.
- Infer T_h from $T_h = (273.16 \text{ K}) \times \frac{Q_h}{Q_c}$

22.5 The Gasoline Engine

Otto cycle

$O \rightarrow A$ Intake stroke
Vol increases from
 $V_2 \rightarrow V_1$

$A \rightarrow B$ Compression stroke

Adiabatic

$V_1 \rightarrow V_2$, $T_A \rightarrow T_B$ (T increase)

Work of compression = area under AB

$B \rightarrow C$ Combustion, Q_h added
 $V \sim$ constant, $P \uparrow$, $T \uparrow$, $W = 0$

$C \rightarrow D$ Power stroke

Adiabatic expansion, $V_2 \rightarrow V_1$

$T \downarrow$, $T_c \rightarrow T_D$

Work of expansion = area under CD

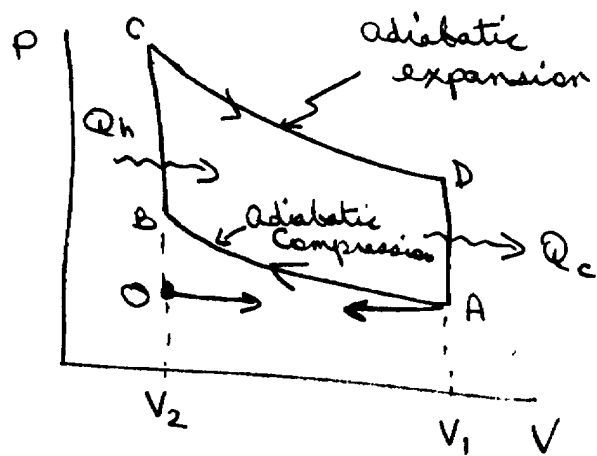
$D \rightarrow A$ Exhaust valves open

$P \downarrow$, V constant, $W = 0$, Q_c removed

$A \rightarrow O$ Exhaust stroke

Residual gas removal

$V \downarrow$, $V_1 \rightarrow V_2$



Example: Efficiency of the Otto Cycle

Assume ideal gas. $\Delta U = 0$ for a cycle.

$$\therefore W = Q_h - Q_c$$

$$Q_h = n C_v (T_c - T_b) \quad (\text{constant volume heat addition})$$

$$Q_c = n C_v (T_d - T_a) \quad (\text{constant volume heat removal})$$

$$\therefore e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{(T_d - T_a)}{(T_c - T_b)}$$

Now since $A \rightarrow B$ + $C \rightarrow D$ are adiabatic:

$$T_A V_1^{\delta-1} = T_B V_2^{\delta-1} \quad , \quad \delta = C_p/C_v \approx 1.4$$

and $T_D V_1^{\delta-1} = T_c V_2^{\delta-1}$

$$\begin{aligned} \therefore \frac{T_D - T_A}{T_c - T_b} &= \frac{T_c (V_2/V_1)^{\delta-1} - T_B (V_2/V_1)^{\delta-1}}{T_D - T_B} \\ &= (V_2/V_1)^{\delta-1} \end{aligned}$$

$$\therefore e = 1 - \frac{1}{(V_1/V_2)^{\delta-1}}$$

V_1/V_2 is called the compression ratio.

$e \uparrow$ as $V_1/V_2 \uparrow$

If $V_1/V_2 = 8$ (typical)

then $e = 56\%$

Actual is $\sim 20\%$ due to friction, heat losses + incomplete combustion.

In terms of temperatures:

$$T_A V_1^{\gamma-1} = T_B V_2^{\gamma-1}$$

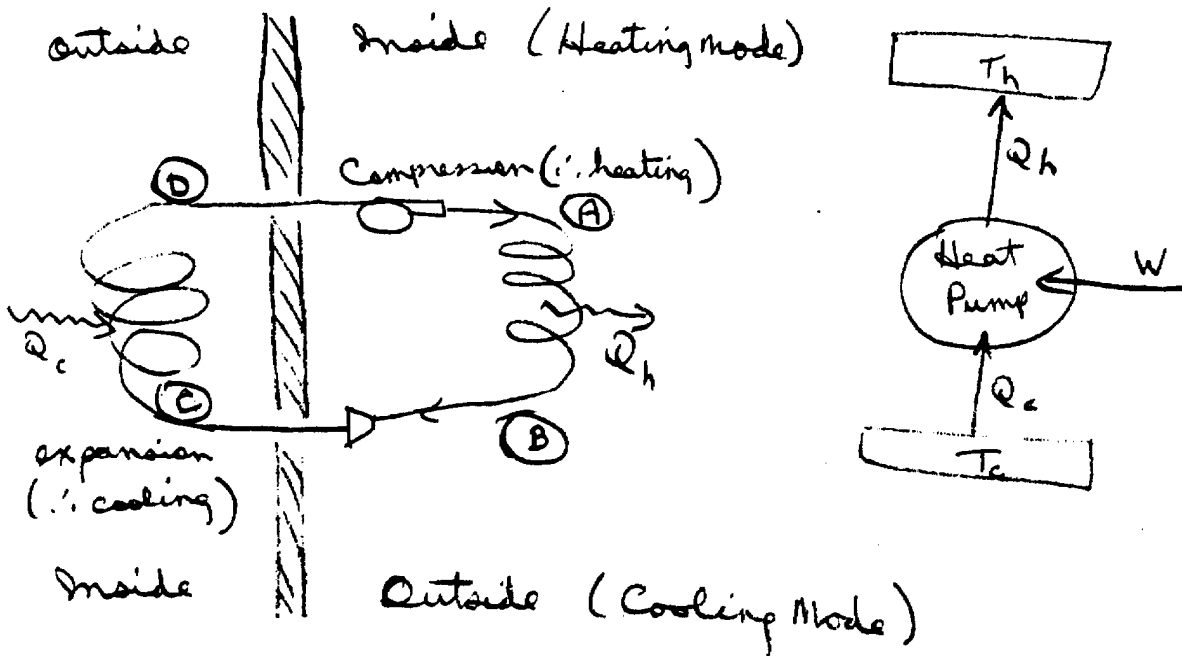
$$\therefore \frac{T_A}{T_B} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_D}{T_C}$$

$$\therefore e = 1 - \frac{T_A}{T_B} = 1 - \frac{T_D}{T_C}$$

Compare to a Carnot cycle:

$$e_{\text{Carnot}} = 1 - \frac{T_{\text{lowest}}}{T_{\text{highest}}} = 1 - \frac{T_A}{T_C} > e_{\text{Otto}}$$

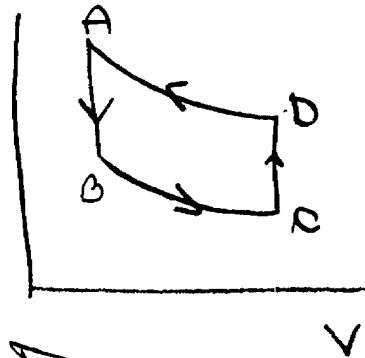
22.6 Heat Pumps and Refrigerators



Carnot cycle in reverse

Coefficient of performance for heat pump

$$\text{COP} \equiv \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}$$



$$\text{COP}_{\text{carnot}} = \text{COP}_{\text{maximum}} = \frac{T_h}{T_h - T_c}$$

typically ~ 4 when $T_c \sim 25^\circ\text{C}$.

$$\text{COP for refrigerator} \equiv \frac{Q_c}{W} \quad (\text{typically } \sim 5 \text{ or } 6)$$

$$\therefore \text{COP}_{\text{max}} (\text{refrigerator}) = \frac{T_c}{T_h - T_c}$$