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Thermodynamics and Statistical Mechanics

Thermodynamics III
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- **Entropy changes in cyclic processes**
- **Maxwell relations**
- **Dissipative work as heat supply**
- **Entropy of ideal gas**
- **Third Law of Thermodynamics**

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT \quad (7)$$

$$W = \int P dV \quad (17)$$

$$C_P = C_V + nR \quad (39)$$

$$C_P = C_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (42)$$

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

$$\delta Q = T dS \quad (79)$$

ENTROPY

Consequence of second law is existence of entropy:

a state function @ thermodynamic equilibrium whose differential is given by

$$\delta Q = T dS \quad (79)$$

S being a state function \rightarrow does not change in any reversible cyclic process:

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

Since Q is extensive \rightarrow so is S

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

CHANGE OF ENTROPY IN IRREVERSIBLE PROCESSES

In non equilibrium states \rightarrow thermodynamic entropy is undefined

If initial and final states of irreversible process are in equilibrium

entropy of these states is defined

so \rightarrow entropy change $\Delta S_{12} = S_2 - S_1$

We can find always reversible process connecting 1 and 2:

equivalent reversible process

Both processes can be joined into irreversible cyclic process

for which Clausius inequality applies and takes the form

$$\int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q_{\text{reversible}}}{T} \leq 0 \quad (80)$$

Since reversible integral is related to change of entropy

$$\int_1^2 \frac{\delta Q_{\text{reversible}}}{T} = \Delta S_{12} \geq \int_1^2 \frac{\delta Q}{T} \quad (81)$$

$$dS \geq \frac{\delta Q}{T} \quad (82)$$

CHANGE OF ENTROPY ON ISOLATED SYSTEMS

If system is isolated $\Rightarrow \delta Q = \delta W = 0$

Still $\Rightarrow dS \geq 0$ due to irreversible processes inside systems
e.g. relaxation to equilibrium

Consider isolated system that consists of two subsystems
each of them at internal equilibrium
but there is no equilibrium between subsystems

Changes in reservoir entropies are:

$$(\Delta S)_{\text{HOT}} = \int_{T \equiv T_2} \frac{\delta Q_{\text{HOT}}}{T} = -\frac{Q_2}{T_2} < 0$$

$$(\Delta S)_{\text{COLD}} = \int_{T \equiv T_1} \frac{\delta Q_{\text{COLD}}}{T} = \frac{Q_1}{T_1} = -\frac{Q_1}{T_1} > 0$$

because hot reservoir loses heat Q_2 to engine
and cold reservoir gains heat Q_1 from engine

ENTROPY CHANGES IN CYCLIC PROCESSES

Then for the whole system follows

$$(\Delta S)_{\text{TOTAL}} = - \left(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \right) \geq 0 \quad (83)$$

According to second law of thermodynamics heat flows from hot to cold body

$$T_1 < T_2$$

Reversible cycle → net change of total entropy of the engine + reservoir is zero

Irreversible cycle → increase of total entropy due to spontaneous processes

MAXWELL RELATION

Inserting (17) and (79) into first law of thermodynamics

main thermodynamic identity

$$dU = TdS - PdV \quad (84)$$

(84) is a differential of internal energy as a function of two variables

Correspondingly \Rightarrow

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad -P = \left(\frac{\partial U}{\partial V} \right)_S \quad (85)$$

As second mixed derivative does not depend on order of differentiation

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \quad (86)$$

it follows that

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad (87)$$

DISSIPATIVE WORK AS HEAT SUPPLY

$$\begin{aligned} \delta Q &= \delta Q_{\text{reversible}} + \delta Q_{\text{dissipative}} & \delta Q_{\text{reversible}} &= TdS \\ \delta W &= \delta W_{\text{reversible}} + \delta W_{\text{dissipative}} & \delta W_{\text{reversible}} &= PdV \end{aligned} \quad \text{and} \quad (88)$$

Then using the first law (25), (84), and (88) we have

$$\delta Q - \delta W = TdS - PdV = \delta Q_{\text{reversible}} - \delta W_{\text{reversible}} \quad (89)$$

It follows that $\Rightarrow \delta Q_{\text{dissipative}} - \delta W_{\text{dissipative}} = 0$

$$\text{or equivalently } \Rightarrow \delta Q - \delta W_{\text{dissipative}} = TdS \quad (90)$$

This shows that dissipative work is equivalent to heat supply

VOLUME DEPENDENCE OF ENTROPY AND INTERNAL ENERGY

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \quad (91)$$

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

to obtain differential of entropy as a function of T and V

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] dV \quad (92)$$

Use uniqueness of mixed second derivatives of S

to obtain a relation involving derivatives of U

(92) implies
$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V = \frac{C_V}{T} \quad (93)$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] \quad (94)$$

INTERNAL ENERGY OF IDEAL GAS

Uniqueness of second mixed derivative of $S(T, V)$ is expressed as

$$\left[\frac{\partial}{\partial V} \frac{1}{T} \left(\frac{\partial U}{\partial T} \right) \right]_V \Big|_T = \left\{ \frac{\partial}{\partial T} \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \right\}_V \quad (95)$$

Performing differentiation

$$\frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2} \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] + \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} + \frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_V \quad (96)$$

Taking into account uniqueness of mixed second derivative of $U(T, V)$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad (97)$$

that is (41)

For the ideal gas from this formula and equation of state follows

$$(\partial U / \partial V)_T = 0 \quad \text{that is} \quad U = U(T)$$

MORE ON MAXWELL RELATIONS

Substituting (97) into (94)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (98)$$

Maxwell relation (98) allows derivation of (97) in a shorter way

From (84) it follows that

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \quad (99)$$

Substituting in (98) yields (97)

THERMODYNAMIC COEFFICIENTS FOR ADIABATIC PROCESSES

Adiabatic compressibility

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (100)$$

To express κ_S through experimentally measurable quantities consider

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad (101)$$

Setting $dS = 0$ and inserting (93) and (98)

$$0 = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV \quad (102)$$

Combining (102) with (7)

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP - \left(\frac{\partial V}{\partial T} \right)_P \frac{T}{C_V} \left(\frac{\partial P}{\partial T} \right)_V dV \quad (103)$$

EQUIVALENTLY...

$$\left[1 + \left(\frac{\partial V}{\partial T} \right)_P \frac{T}{C_V} \left(\frac{\partial P}{\partial T} \right)_V \right] dV = \left(\frac{\partial V}{\partial P} \right)_T dP \quad (104)$$

(105) can be simplified with help of (42) to $\gamma dV = \left(\frac{\partial V}{\partial P} \right)_T dP$ (105)

Adiabatic compressibility $\Rightarrow \kappa_S = \frac{\kappa_T}{\gamma}$ (106)

Since $C_P > C_V$ for all substances $\kappa_S < \kappa_T$ is universally valid

Adiabatic compression is accompanied by temperature increase

that is described by thermodynamic coefficient $(\partial T / \partial P)_S$

Combining (102) and (105)

$$-\frac{C_V}{T} dT = \left(\frac{\partial P}{\partial T} \right)_V \frac{C_V}{C_P} \left(\frac{\partial V}{\partial P} \right)_T dP \quad (107)$$

THIS YIELDS...

$$\left(\frac{\partial T}{dP}\right)_S = -\frac{T}{C_P} \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \quad (108)$$

With help of (13) this simplifies to

$$\left(\frac{\partial T}{dP}\right)_S = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P = \frac{VT\beta}{C_P} \quad (109)$$

For ideal gas $T\beta = 1$ and this formula gives

$$\left(\frac{\partial T}{dP}\right)_S = \frac{T}{C_P} \frac{nR}{P} = \frac{V}{C_P} \quad (110)$$

Adiabat equation of ideal gas in the form of (53) can be rewritten as

$$T = AP^{1-1/\gamma} \quad A = \text{const} \quad (111)$$

Differentiating this equation

$$\left(\frac{\partial T}{dP}\right)_S = A \left(1 - \frac{1}{\gamma}\right) P^{-1/\gamma} = \left(1 - \frac{1}{\gamma}\right) \frac{T}{P} = \left(1 - \frac{1}{\gamma}\right) \frac{V}{nR} \quad (112)$$

ENTROPY OF IDEAL GAS

Energy of ideal gas depends on temperature only $U = U(T)$

For perfect gas $\Rightarrow C_V = \text{const}$ and (93) can be integrated over T

$$S(T, V) = C_V \ln T + f(V) \quad (113)$$

Using (98)

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{P}{T} = \frac{nR}{V} \quad (114)$$

Inserting $S(T, V)$ into (114) $\Rightarrow df/dV = nR/V$

Integration yields $\Rightarrow f = nR \ln V + S_0$

Then with help of (50) one obtains

$$S = C_V \ln T + nR \ln V + S_0 = C_V \ln (TV^{\gamma-1}) + S_0$$

This formula defines entropy up to an arbitrary constant S_0

In adiabatic process of a perfect gas $TV^{\gamma-1} = \text{const}$
and entropy does not change

THIRD LAW OF THERMODYNAMICS

Analyzing experimental data Walther Nernst concluded that

in the limit $T \rightarrow 0$ entropy becomes constant
independent of other thermodynamic parameters such as volume and pressure

$$\left(\frac{\partial S}{\partial V} \right)_{T \rightarrow 0} = \left(\frac{\partial S}{\partial P} \right)_{T \rightarrow 0} = 0 \quad (117)$$

Since in thermodynamics entropy is defined up to a constant

Planck has suggested to define $S(T \rightarrow 0) = 0$ (118)

Explanation of these results is possible only within statistical physics
It turns out that statistically defined entropy always satisfies (117)
whereas (118) holds for most substances

Some materials have a degenerate ground state

and in this case entropy tends to a finite constant at $T \rightarrow 0$

CONSEQUENCES OF THE THIRD LAW

Integrating (93) one obtains $\Rightarrow S = \int_0^T \frac{C_V}{T} dT + S_0$ (119)

If C_V is finite at $T \rightarrow 0$ entropy logarithmically diverges

$$\text{contradicting third law} \Rightarrow C_V(T \rightarrow 0) = 0 \quad (120)$$

Same condition for C_P can be proved in a similar way

Note that divergence of entropy of ideal gas (115) at $T \rightarrow 0$

only proves that concept of ideal gas breaks down at low temperatures where gases become liquid and solid

From (98) \Rightarrow pressure thermal coefficient vanishes at absolute zero

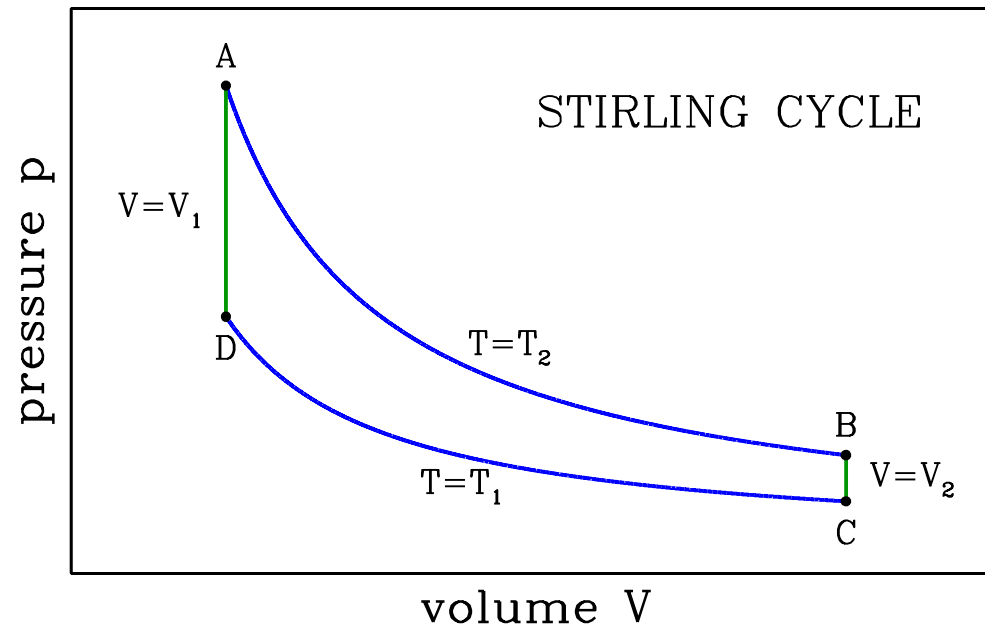
$$\left(\frac{\partial P}{\partial T} \right)_V \Big|_{T \rightarrow 0} = 0 \quad (121)$$

Next class we will see that thermal expansion coefficient also vanishes:

$$\left(\frac{\partial V}{\partial T} \right)_P \Big|_{T \rightarrow 0} = 0 \quad (122)$$

THE STIRLING CYCLE

Consists of two **isotherms** and two **isochores**



Isothermal ideal gas equation of state $\rightarrow d(pV) = 0$

$$P_A V_1 = P_B V_2$$

and

$$P_D V_1 = P_C V_2$$

$$\frac{P_B}{P_A} = \frac{P_C}{P_D} = \frac{V_1}{V_2}$$

THE STIRLING CYCLE II

AB : This isothermal expansion is the power stroke

For n moles of ideal gas throughout

$$PV = nRT_2 = P_1V_1 \Rightarrow W_{AB} = \int_{V_1}^{V_2} dV \frac{nRT_2}{V} = nRT_2 \ln \left(\frac{V_2}{V_1} \right)$$

Since *AB* is isotherm $\Rightarrow U_A = U_B \Rightarrow \Delta U_{AB} = 0 \Rightarrow Q_{AB} = W_{AB}$

BC : isochoric cooling

$$dV = 0 \Rightarrow W_{BC} = 0$$

$$\Delta U_{BC} = U_C - U_B = \int_{T_2}^{T_1} C_V dT = C_V (T_1 - T_2) < 0$$

Since $W_{BC} = 0 \Rightarrow Q_{BC} = \Delta U_{BC}$

THE STIRLING CYCLE III

CD : Isothermal compression

$$W_{CD} = \int_{V_2}^{V_1} dV \frac{nRT_1}{V} = -nRT_1 \ln \left(\frac{V_2}{V_1} \right)$$

Since *CD* is isotherm $\Rightarrow U_C = U_D \Rightarrow \Delta U_{CD} = 0 \Rightarrow Q_{CD} = W_{CD}$

DA : Isochoric heating

$$dV = 0 \Rightarrow W_{DA} = 0$$

$$\Delta U_{DA} = U_A - U_D = C_V(T_2 - T_1) > 0$$

Since $W_{DA} = 0 \Rightarrow Q_{DA} = \Delta U_{DA}$

We now add up all work contributions to obtain

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = nR(T_2 - T_1) \ln \left(\frac{V_2}{V_1} \right)$$

$$\text{Cycle efficiency} \Rightarrow \eta = \frac{W}{Q_{AB} + Q_{DA}} = \frac{T_2 - T_1}{T_2 + C_V(T_2 - T_1)/[nR \ln(V_B/V_A)]}$$

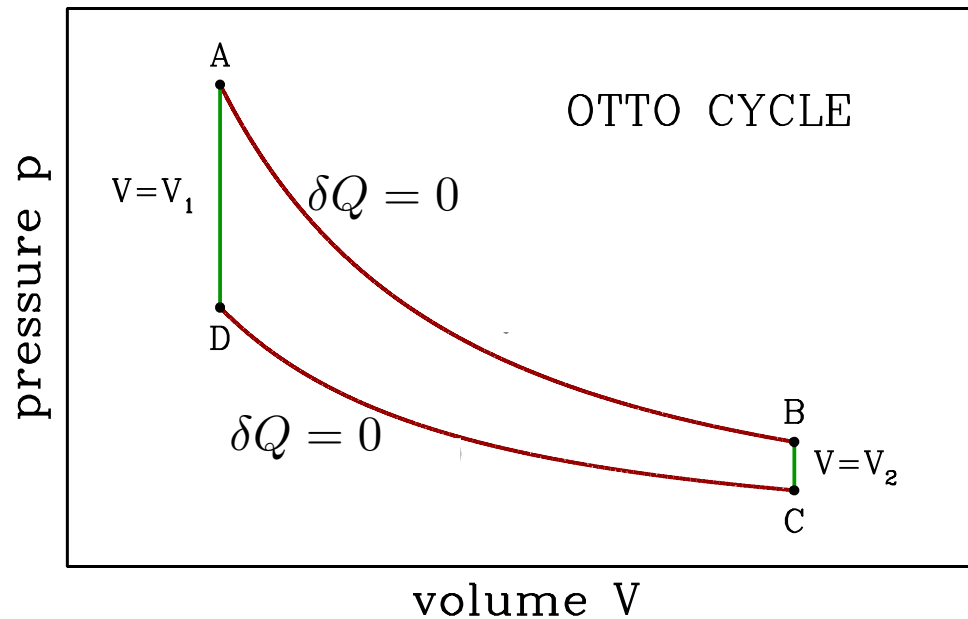
Because of the additional positive term on the denominator

efficiency is smaller than the efficiency of the Carnot cycle

THE OTTO AND DIESEL CYCLES

Otto cycle is rough approximation to physics of gasoline engine

Consists of two **adiabats** and two **isochores**



Assuming ideal gas along adiabats $\rightarrow d(pV^\gamma) = 0$

$$P_A V_1^\gamma = P_B V_2^\gamma \quad \text{and} \quad P_D V_1^\gamma = P_C V_2^\gamma$$

$$\frac{P_B}{P_A} = \frac{P_C}{P_D} = \left(\frac{V_1}{V_2}\right)^\gamma$$

THE OTTO AND DIESEL CYCLES II

AB : Adiabatic expansion (power stroke)

$$Q_{AB} = 0 \Rightarrow W_{AB} = -\Delta U_{AB} = U_A - U_B$$

$$W_{AB} = \frac{P_A V_1 - P_B V_2}{\gamma - 1} = \frac{P_A V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \right]$$

Equivalently \rightarrow using adiabatic equation of state

$$W_{AB} = \int_{V_1}^{V_2} P dV = P_A V_1^\gamma \int_{V_1}^{V_2} dV v^{-\gamma} = \frac{P_A V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \right]$$

BC : Isochoric cooling (exhaust)

$$dV = 0 \Rightarrow W_{BC} = 0$$

heat absorbed $\rightarrow Q_{BC} = U_C - U_B = C_V(T_2 - T_1) = \frac{V_2}{\gamma - 1}(P_C - P_B)$

In realistic engine

this is stage in which old burned gas is ejected and new gas is inserted

THE OTTO AND DIESEL CYCLES III

***CD* : adiabatic compression** $Q_{CD} = 0 \Rightarrow W_{CD} = U_C - U_D$

$$W_{CD} = \frac{P_C V_2 - P_D V_1}{\gamma - 1} = -\frac{P_D V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \right]$$

***DA* : isochoric heating (combustion of the gas)**

$$dV = 0 \Rightarrow W_{DA} = 0$$

heat absorbed by gas

$$Q_{DA} = U_A - U_D = \frac{V_1}{\gamma - 1} (P_A - P_D)$$

total work done per cycle

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = \frac{(P_A - P_D)V_1}{\gamma - 1} \left[1 - \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \right]$$

efficiency

$$\eta \equiv \frac{W}{Q_{DA}} = 1 - \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$

THE OTTO AND DIESEL CYCLES IV

Ratio $r = V_2/V_1$ → compression ratio

Otto cycle becomes more efficient simply by increasing compression ratio

Problem with this scheme is that

if fuel mixture becomes too hot → it will spontaneously 'preignite'
and pressure will jump up before point D in cycle is reached

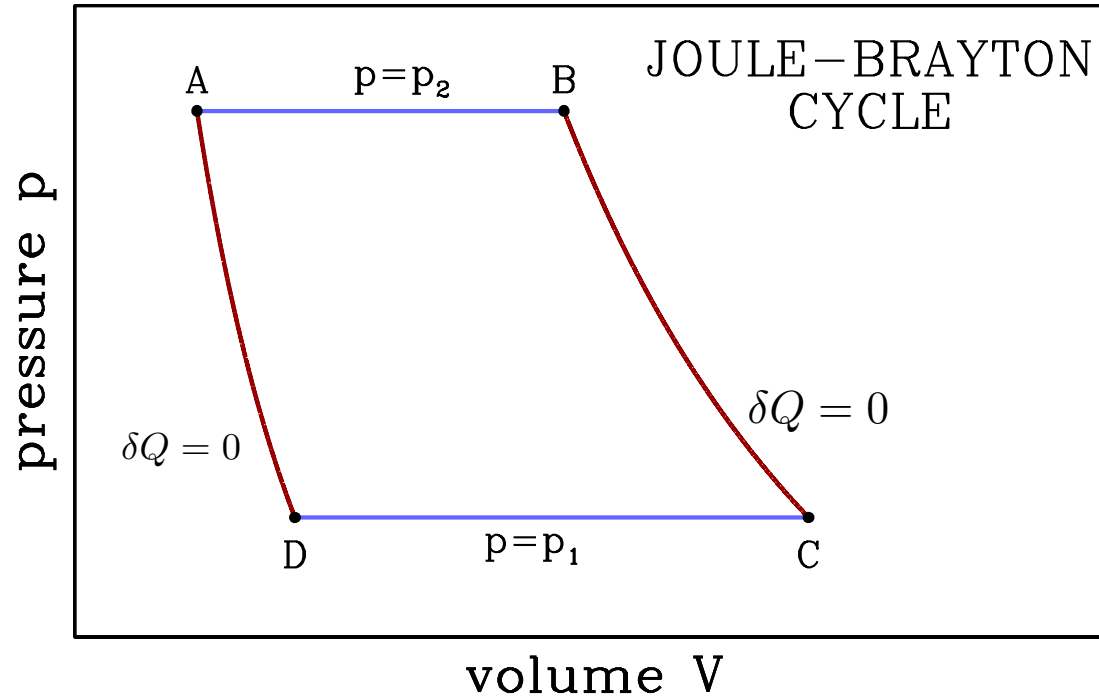
Diesel engine avoids preignition by compressing air only
and then later spraying fuel into cylinder
when air temperature is sufficient for fuel ignition

Rate at which fuel is injected is adjusted
so that the ignition process takes place at constant pressure

Diesel engine → step DA is isobaric

JOULE-BRAYTON CYCLE

Consists of two **adiabats** and two **isobars**



Along adiabats we have

$$P_2 V_A^\gamma = P_1 V_D^\gamma$$

and

$$P_2 V_B^\gamma = P_1 V_C^\gamma$$

$$\frac{V_D}{V_A} = \frac{V_C}{V_B} = \left(\frac{P_2}{P_1} \right)^{\frac{1}{\gamma}}$$

JOULE-BRAYTON CYCLE II

AB : Isobaric expansion

$$W_{AB} = \int_{V_A}^{V_B} P_2 dV = P_2(V_B - V_A)$$

$$\Delta U_{AB} = U_B - U_A = \frac{P_2(V_B - V_A)}{\gamma - 1}$$

$$Q_{AB} = \Delta U_{AB} + W_{AB} = \frac{\gamma P_2(V_B - V_A)}{\gamma - 1}$$

BC : Adiabatic expansion

$$Q_{BC} = 0 \Rightarrow W_{BC} = U_B - U_C$$

work done by the gas is:

$$W_{BC} = \frac{P_2 V_B - P_1 V_C}{\gamma - 1} = \frac{P_2 V_B}{\gamma - 1} \left(1 - \frac{P_1 V_C}{P_2 V_B} \right) = \frac{P_2 V_B}{\gamma - 1} \left[1 - \left(\frac{P_1}{P_2} \right)^{1-\gamma^{-1}} \right]$$

JOULE-BRAYTON CYCLE III

CD : Isobaric compression

$$W_{CD} = \int_{V_C}^{V_D} P_1 dV = P_1(V_D - V_C) = -P_2(V_B - V_A) \left(\frac{P_1}{P_2}\right)^{1-\gamma^{-1}}$$

$$\Delta U_{CD} = U_D - U_C = \frac{P_1(V_D - V_C)}{\gamma - 1}$$

$$Q_{CD} = \Delta U_{CD} + W_{CD} = -\frac{\gamma P_2}{\gamma - 1}(V_B - V_A) \left(\frac{P_1}{P_2}\right)^{1-\gamma^{-1}}$$

DA : Adiabatic compression

$$Q_{DA} = 0 \Rightarrow W_{DA} = U_D - U_A$$

$$W_{DA} = \frac{P_1 V_D - P_2 V_A}{\gamma - 1} = -\frac{P_2 V_A}{\gamma - 1} \left(1 - \frac{P_1 V_D}{P_2 V_A}\right) = -\frac{P_2 V_A}{\gamma - 1} \left[1 - \left(\frac{P_1}{P_2}\right)^{1-\gamma^{-1}}\right]$$

JOULE-BRAYTON CYCLE IV

Total work done per cycle:

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = -\frac{\gamma P_2 (V_B - V_A)}{\gamma - 1} \left[1 - \left(\frac{P_1}{P_2} \right)^{1-\gamma^{-1}} \right]$$

Cycle efficiency \rightarrow

$$\eta \equiv \frac{W}{Q_{AB}} = 1 - \left(\frac{P_1}{P_2} \right)^{1-\gamma^{-1}}$$