



Lecture 2

1ST Law of Thermodynamics

- 1ST Law
- Thermodynamic Processes
- Heat capacities

Objectives

- Explain 1ST Law, its significance and limitations
- Explain various thermodynamic processes.



Introduction



A Donkey is an engine: It eats (= heat input) to get energy in order to work **-Concept of 1ST Law**



2/14/2020 10:27 AM

FWN_UoN

3

■ **RECAL:**

Energy may be converted from one form to another e.g., heat to work but **TOTAL ENERGY MUST BE CONSERVED**



2/14/2020 10:27 AM

FWN_UoN

4

1ST Law of Thermodynamics

- Defines relationship between heat (dQ), work (dW) & internal energy (dU) of a system by mandating **conservation of energy**.



2/14/2020 10:27 AM

FWN_UoN

5

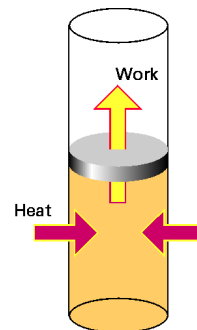
$$dQ = dU + dW$$

1ST Law

Work done by (or on) system

Change in internal energy

Heat flow
into/out of system



2/14/2020 10:27 AM

FWN_UoN

6

1ST Law Simplified

$$dQ = dU + dW$$

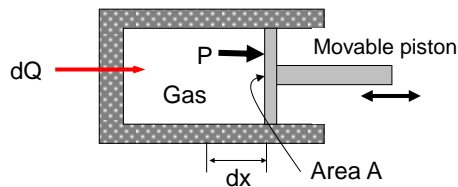
"We eat in order to work"

Or

"No animal works continuously without eating or wearing out"



- For mechanical device e.g., gas in cylinder



$$dW = F \cdot dx = PA \cdot dx$$

- $\Rightarrow dW = P(Adx) = PdV$

- $\Rightarrow dQ = dU + PdV \dots\dots\dots(2)$



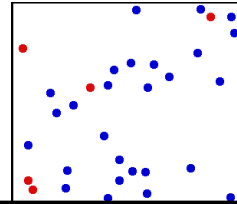
Internal Energy of Ideal Gas

- From Kinetic Theory of gases, internal energy (**U**) of ideal gas with **f** degrees of freedom is:

$$U = \frac{f}{2} RT = \frac{f}{2} NK_B T \quad \dots\dots\dots(1)$$

$f \Rightarrow 3$ (monatomic), 5 (diatomic) etc

- f** = translational & rotational degrees of freedom. Vibrational ones are negligible



2/14/2020 10:27 AM

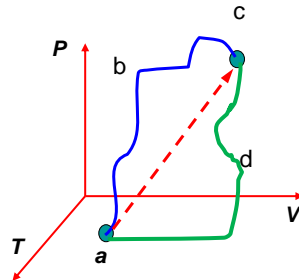
FWN_UoN

Note

- U** is a **state function** i.e., it does not depend on the **path taken/process**

$$dU_{abc} = dU_{adc} \quad \text{S.T} \quad \oint_C dU = 0$$

- U** depends only on **T**
- For reversible process, **dU = 0**



2/14/2020 10:27 AM

FWN_UoN

10

- **dQ & dW** are path dependent & *are not state functions* S.T $dW_{abc} \neq dW_{adc}$

- $\Rightarrow \oint_C dW \neq 0 \quad \& \quad \oint_C dQ \neq 0$



Significance of 1ST Law

- It provides means of determining **dU**

Limitations of 1ST Law

- Does not define efficiency of systems i.e., how much **dQ** is converted into **dW**



Perpetual Machines of 1st kind

- A machine that works continuously without energy input (dQ) or change in (dU) does not exist.



Worked Example

- A device working reversibly takes in 1000 J of heat, ejects 200 J of heat to a cold reservoir and produces 800 J of work.

Does this device violate 1ST Law ?



Soln

(i) 1ST Law mandates conservation of Energy

■ Since system is reversible $\Rightarrow dU = 0$

$$\therefore dW = dQ$$

$$\Rightarrow W (800) = Q_h (1000) - Q_c (200) = 800J$$

\Rightarrow device doesn't violate 1ST Law since no energy is created nor destroyed.



2/14/2020 10:27 AM

FWN_UoN

15

Thermodynamics and Laws of nature Rule of Nature: We eat to live

Laws of Nature	Laws of Thermodynamics
1. We eat when hungry	Zeroth Law: Heat flows from hot to Cold
2. We eat in order to work	1st Law: $dQ = dU + dW$



2/14/2020 10:27 AM

--

Lecture Evaluation



- State 1ST Law giving its significance and limitations
- Explain perpetual machines of 1ST Kind



2/14/2020 10:27 AM

FWN_UoN

17



Thermodynamic processes

- **Process** = passage of a system from an initial to a final state of equilibrium as a result of transfers of heat, work or Internal Energy
- An ideal gas can undergo **4** main Processes:-
 - **isothermal** (heat transfer at const temp)
 - **isobaric** (const P)
 - **isochoric** (const V) and
 - **adiabatic** (no heat input)

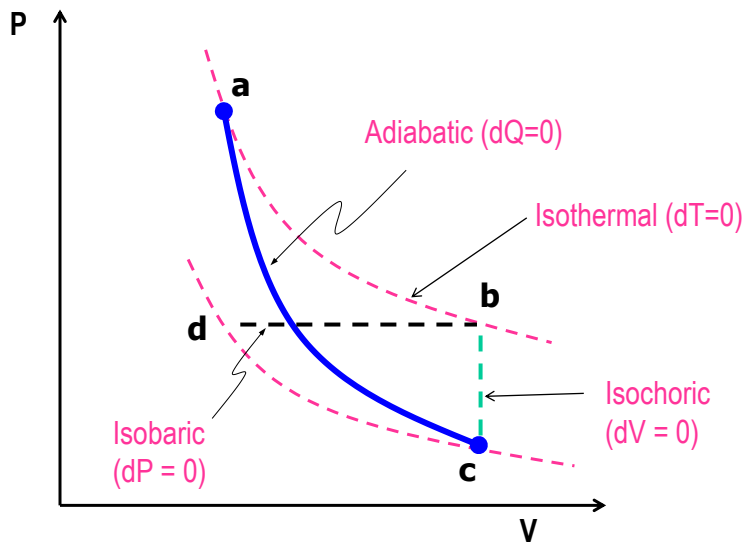


□ Other Processes

- **Reversible process** → the system is close to equilibrium at all times. **NB.** there are no truly reversible processes in nature.
- **Cyclic process** → the final and initial state are the same.



- These processes can be represented on **P-V diagram**



2/14/2020 10:27 AM

FWN_UoN

21

Applications of 1ST Law

- Used to find work done in various thermodynamic processes for purposes of designing a (heat engine) with max possible efficiency



2/14/2020 10:27 AM

FWN_UoN

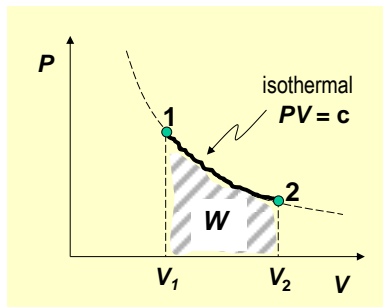
22

(a) Isothermal process ($dT = 0$)

- Work done = area under P-V curve i.e.,

$$W_{1 \rightarrow 2} = \int_{V_1}^{V_2} P dV \quad \text{but } P = \frac{nRT}{V}$$

$$\begin{aligned} \Rightarrow W &= nRT \int_{V_1}^{V_2} \frac{dV}{V} \\ &= nRT \ln \frac{V_2}{V_1} \end{aligned}$$



- Also since $P_1V_1 = P_2V_2 \Rightarrow W = nRT \ln \frac{P_1}{P_2}$



2/14/2020 10:27 AM

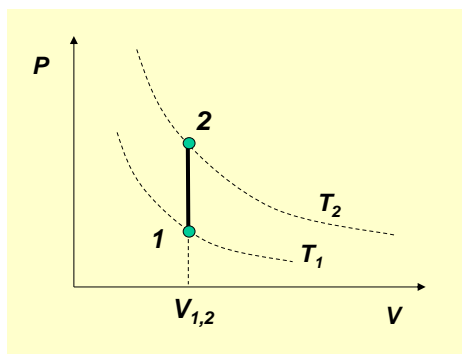
FWN_UoN

23

(b) Isochoric Process ($dV = 0$)

$$W_{1 \rightarrow 2} = \int_1^2 P dV = 0 \Rightarrow \text{heat input only increases } dU$$

$$dQ = dU = \frac{3}{2} R dT \quad \text{for monoatomic gas}$$



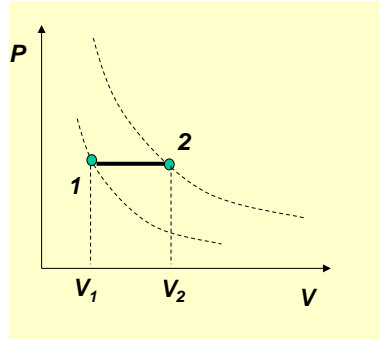
2/14/2020 10:27 AM

FWN_UoN

24

(c) Isobaric process ($dP = 0$)

$$W_{1 \rightarrow 2} = \int_1^2 P dV = P(V_2 - V_1) < 0$$



- 1ST Law becomes:
 $dQ = dU + PdV = dH$

Where dH = Entalpy = heat involved in chemical reaction (at const P)



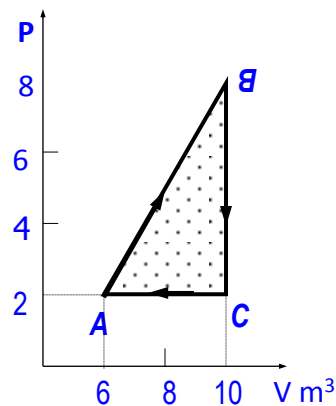
2/14/2020 10:27 AM

FWN_UoN

25

Worked Example

- An ideal gas is taken through cyclic process ABCA. Determine
 - (i) Net heat transferred to system during one complete cycle
 - (ii) Net heat input for reversed cycle ACBA.



2/14/2020 10:27 AM

FWN_UoN

26

Soln

(i) From first law, $dQ = dU + dW$

■ But $dW = PdV = \text{area under P-V}$
 $dU = 0$ in cyclic process.

■ $\Rightarrow dQ = PdV = \frac{1}{2}(8-2)(4) = 12 \text{ KJ}$

(ii) dQ is the same as in (i)



2/14/2020 10:27 AM

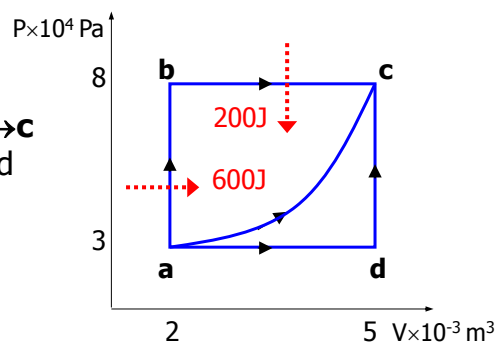
FWN_UoN

27

Activity 2

■ An Ideal gas is taken from state **a** to **c** either through **a**→**b**→**c** or **a**→**d**→**c**. In processes **a**→**b** and **b**→**c**, 600 J and 200J are given to the system respectively. Calculate

- dU along **a**→**b**
- dU along **a**→**b**→**c**
- Total heat added in **a**→**d**→**c**



2/14/2020 10:27 AM

FWN_UoN

28

Solution

From 1ST Law ($dU = dQ - dW$)

- (i) \Rightarrow Along $\mathbf{a \rightarrow b}$, $dW = 0$: $\Rightarrow dU = dQ = 600 \text{ J}$
 (ii) Total dQ along $\mathbf{a \rightarrow b \rightarrow c} = (600 + 200) = 800 \text{ J}$

$$\begin{aligned} dW \text{ along } \mathbf{a \rightarrow b} &= 0 \\ dW \text{ along } \mathbf{b \rightarrow c} &= PdV \\ &= (8 \times 10^4 \text{ Pa})(3 \times 10^{-3} \text{ m}^3) = 240 \text{ J}. \end{aligned}$$

$$\begin{aligned} \Rightarrow \text{Total } dW \text{ along } \mathbf{a \rightarrow b \rightarrow c} &= 240 \text{ J} \\ \therefore dU \text{ along } \mathbf{a \rightarrow b \rightarrow c} &= dQ - dW \\ &= (800 - 240) \text{ J} = 560 \text{ J} \end{aligned}$$



2/14/2020 10:27 AM

FWN_UoN

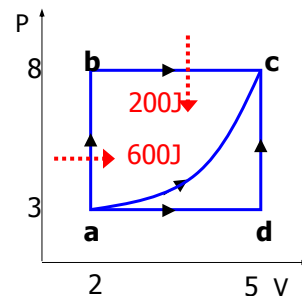
29

- (iii) Along $\mathbf{a \rightarrow d \rightarrow c}$, $dU = 560 \text{ J}$

(NB. dU is a state function S.T total dU along $\mathbf{a \rightarrow b \rightarrow c} = dU$ along $\mathbf{a \rightarrow d \rightarrow c}$.)

$$\begin{aligned} dW \text{ along } \mathbf{a \rightarrow d \rightarrow c} \\ &= P_1(V_2 - V_1) = 90 \text{ J} \end{aligned}$$

$$\begin{aligned} \text{NB. along } \mathbf{d \rightarrow c}, dW &= 0 \\ \Rightarrow \text{Total } dQ \text{ in } \mathbf{a \rightarrow d \rightarrow c} \\ &= dU + dW \\ &= (560 + 90) \text{ J} = 650 \text{ J}. \end{aligned}$$



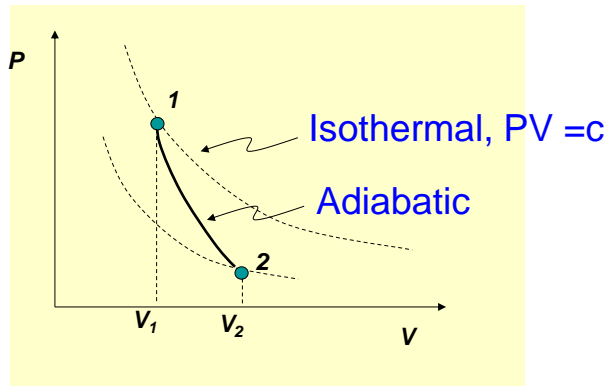
2/14/2020 10:27 AM

FWN_UoN

30

(d) Adiabatic process ($dQ = 0$)

- No heat enters or leaves the system BUT *gas expands doing work* (dW) as dU decreases with decrease in T (path 1-2)



2/14/2020 10:27 AM

FWN_UoW

31

$$\Rightarrow PdV + dU = 0 \quad \text{Form of 1}^{st} \text{ Law.....(1)}$$

- But $dU = \frac{3}{2} RdT = \alpha RdT \quad \text{.....(2)}$

$$\Rightarrow PdV + \alpha RdT = 0 \quad \text{.....(3)}$$

- To obtain dW , we first need to obtain **Eqn for adiabatic process** by substituting for dT in terms P and V in eqn (3).
- From the ideal gas law ($PV = nRT$), differentiating we have

$$PdV + VdP = RdT$$



2/14/2020 10:27 AM

FWN_UoW

32

$$\Rightarrow dT = \left(\frac{PdV + VdP}{R} \right)$$

- Substituting for dT in (3), gives

$$PdV + \alpha(PdV + VdP) = 0$$

$$\Rightarrow (1 + \alpha)PdV = -\alpha VdP$$

- Integrating we have

$$(\alpha + 1) \int \frac{dV}{V} = -\alpha \int \frac{dP}{P}$$

$$\Rightarrow \left(\frac{\alpha + 1}{\alpha} \right) \ln V = -\ln P + c$$



$$\Rightarrow \ln(PV^\gamma) = c \quad \text{where } \gamma = \left(\frac{\alpha + 1}{\alpha} \right) = \frac{5}{2}$$

$$\Rightarrow PV^\gamma = c \quad \text{Eqn for Adiabatic.....(5)}$$

- \Rightarrow Adiabatic curve has steeper slope (γ times) than isothermal curve



Activity

- Show also that for adiabatic process

$$(i) \quad TV^\gamma = c$$

$$(ii) \quad TP^{\left(\frac{1-\gamma}{\gamma}\right)} = c$$



Soln

- From $PV^\gamma = c$
- Replacing for P from ideal gas Eqn ($PV = nRT$)

$$\Rightarrow \left(\frac{nRT_1/V_1}{nRT_2/V_2} \right) = \frac{V_2^\gamma}{V_1^\gamma}$$

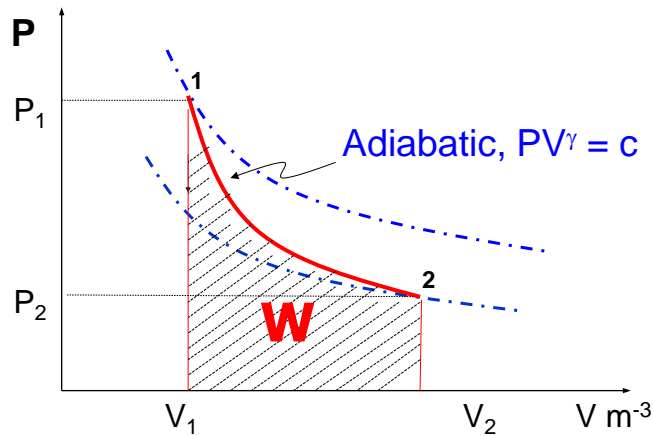
$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\Rightarrow TV^{\gamma-1} = c$$



Work done in adiabatic Process

- W = area under $PV^\gamma = c$ curve



2/14/2020 10:27 AM

FWN_UoN

37

- $$\Rightarrow W = \int_{V_1}^{V_2} P dV = C \int_{V_1}^{V_2} \frac{dV}{V^\gamma} \quad \text{since } P = \frac{C}{V^\gamma}$$

$$\Rightarrow W = \frac{1}{1-\gamma} \left(\frac{C}{V_2^{\gamma-1}} - \frac{C}{V_1^{\gamma-1}} \right)$$

- But $P_1 V_1^\gamma = P_2 V_2^\gamma = C$. Replacing c we get

$$W = \frac{1}{1-\gamma} \left(\frac{P_2 V_2^\gamma}{V_2^\gamma} - \frac{P_1 V_1^\gamma}{V_1^\gamma} \right)$$

$$\Rightarrow W = \left(\frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \right)$$



2/14/2020 10:27 AM

FWN_UoN

38

Alternatively

$$dW = \int_{V_1}^{V_2} PdV = -dU = -\frac{3}{2}R \int_{T_1}^{T_2} dT. \quad \text{for } n = 1$$
$$= -\frac{3}{2}R(T_2 - T_1) = \frac{3}{2}R(T_1 - T_2)$$

- Substituting for T_1 and T_2 from $PV = nRT$, we get

$$dW = \frac{3}{2}R \left(\frac{P_1V_1}{R} - \frac{P_2V_2}{R} \right) = \left(\frac{P_1V_1 - P_2V_2}{\gamma - 1} \right)$$



2/14/2020 10:27 AM

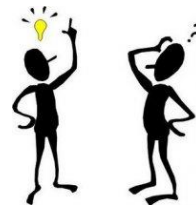
FWN_UoN

39

Activity

- Show that W can also be given by

$$(i) \quad W = \frac{R}{\gamma - 1} (T_1 - T_2)$$



2/14/2020 10:27 AM

FWN_UoN

40

Soln

(i) From $PV^\gamma = P_1V_1^\gamma = \text{const}$

$$\begin{aligned}W_{1 \rightarrow 2} &= -\int_{V_1}^{V_2} P(V, T) dV = -\int_{V_1}^{V_2} \frac{P_1V_1^\gamma}{V^\gamma} dV = -P_1V_1^\gamma \frac{1}{-\gamma+1} V^{-\gamma+1} \Big|_{V_1}^{V_2} \\ &= P_1V_1^\gamma \frac{1}{\gamma-1} \left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right)\end{aligned}$$



Examples of Adiabatic processes

- Adiabatic processes take place rapidly e.g.,
 - (i) *Air compressor*
 - Air let out from an air compressor feels cold

(ii) *Opening a bottle of carbonated beverage*



Activity

- A gas is rapidly compressed from initial pressure is 10^5 Pa and temperature of 22°C ($= 295$ K) to a volume that is a quarter of its original volume (e.g., pumping bike's tire). Find the final temperature?



Soln

- From $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} = c$

$$\Rightarrow T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 514 \text{ K}$$



Activity 2.4

- During the ascent of a meteorological helium-gas balloon, its volume increases from $V_i = 1 \text{ m}^3$ to $V_f = 1.8 \text{ m}^3$, and pressure inside balloon decreases linearly from 1 bar ($=10^5 \text{ N/m}^2$) to 0.5 bar.

(a) If initial T is 300K, find the final T ?
(b) How much work is done *by* the gas?
(c) How much "heat" does the gas absorb?



2/14/2020 10:27 AM

FWN_UoN

45

Lecture -Evaluation



- Explain the following Processes –
Isothermal, Isobaric, Isochoric, Adiabatic
- State Eqns of state for Isothermal & Adiabatic & give expressions for work done in these processes
- List some applications of Adiabatic process



2/14/2020 10:27 AM

FWN_UoN

46



2.3

Heat Capacities of Ideal Gas

- Heat absorbed by a system (dQ) is measure by its capacity to absorb heat i.e., its heat capacity (C).

- The heat capacity of a system is the amount of heat energy required to produce a unit temperature rise in that system

$$C = \left(\frac{dQ}{dT} \right)$$



- NB. Heat can be added to a system either at **const Pressure (P)** or **constant Volume (V)**
- For a constant volume process, the **specific heat capacity (C_V)** is:- (NB $dW = 0$)

$$C_V = \left(\frac{dQ}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V = \frac{3}{2} R \quad \dots\dots\dots(1)$$



- If dQ is added at **constant pressure**, then **specific heat capacity at const P (C_P)** is

$$C_P = \left(\frac{dQ}{dT} \right)_P = \left(\frac{dU + PdV}{dT} \right)_P$$

- But from $(PV = nRT) \Rightarrow$

$$C_P = \frac{dU}{dT} + \frac{nRdT}{dT} = C_V + R \quad \dots\dots\dots(2)$$

- \Rightarrow **$C_p - C_v = R$ Mayer's relation**



Ratio of heat Capacities

$$\frac{C_P}{C_V} = \gamma = 1.67 \quad \text{..... The Gamma relation (3)}$$



Summary

$$C = \frac{\delta Q}{dT} = \frac{dU + PdV}{dT}$$

$V = \text{const}$ \rightarrow $C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2}R$

$P = \text{const}$ \rightarrow $C_P = \left(\frac{\partial H}{\partial T} \right)_P = C_V + R$



[Lecture -Evaluation]



- Explain C_p and C_v
- Why is $C_p > C_v$ always ?



2/14/2020 10:27 AM

FWN_UoN

53



2/14/2020 10:27 AM

FWN_UoN

54