

Thermodynamics

Lecture 3 (Content)

- Evaluation of a perfect/exact differential quantity
- Understanding “Work” under different thermodynamic conditions
- Closed system → Reversible and irreversible isothermal condition
 - Comparison

Lecture 4 (Content)

- Understanding “Work” under different thermodynamic conditions
- Isolated system → Reversible and irreversible adiabatic condition
 - T,V,P relations under adiabatic condition
 - Evaluation of final equilibrium state from any initial input
 - Evaluation and comparison of workdone
 - Applications

Perfect differentials:-

Let us consider a quantity 'z' whose value is determined solely by two other variables x and y at any moment, in any given state, that is, if x & y are given a particular value, the value of 'z' is thereby fixed. If x & y vary, then z will also vary. Thus, mathematically, if we consider $z = f(x, y)$, the change of z can be estimated provided the derivative of the function z w.r.t. x and y are known. Formal derivatives are

* $\left(\frac{\partial z}{\partial x}\right)_y =$ rate of change of 'z' with respect to x at const y

dependent variable

Independent variable

* $\left(\frac{\partial z}{\partial y}\right)_x = \dots$ " " " " \downarrow variable " " \downarrow variable at const x

if x & y both change simultaneously, the total change is expressed as,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\Rightarrow dz = M(x, y) dx + N(x, y) dy$$

where $M(x, y) = \left(\frac{\partial z}{\partial x} \right)_y$ and $N(x, y) = \left(\frac{\partial z}{\partial y} \right)_x$

* Conditions for Exactness:-

For a differential $M(x, y)dx + N(x, y)dy$ to be exact, it must satisfy the following relation (which is mathematically known as Schwarz's theorem; also called the cross partial derivative test):

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \Rightarrow \frac{\partial^2 Z}{\partial x \partial y} = \frac{\partial^2 Z}{\partial y \partial x}$$

\Rightarrow This ensures M, N come from a common potential function $Z = f(x, y)$.

Example:- Consider the differential expression:

$$dZ = (2xy)dx + (x^2 + 3y^2)dy$$

Here, $M = 2xy$ and $N = x^2 + 3y^2$

Performing cross partial derivative test:-

$$\frac{\partial M}{\partial y} = \frac{\partial}{\partial y} (2xy) = 2x$$

$$\frac{\partial N}{\partial x} = \frac{\partial}{\partial x} (x^2 + 3y^2) = 2x$$

Since, $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$, the differential 'dZ' is exact.

This means there exists a function $Z(x, y)$ such that

$$\frac{\partial Z}{\partial x} = 2xy, \quad \frac{\partial Z}{\partial y} = x^2 + 3y^2$$

$$\frac{\partial Z}{\partial x} = 2xy, \quad \frac{\partial Z}{\partial y} = x^2 + 3y^2$$

Integrating $\frac{\partial u}{\partial x}$ w.r.t. x :

$$Z(x, y) = \int 2xy \, dx = x^2 y + g(y)$$

To determine $g(y)$, differentiate w.r.t. y :

$$\frac{\partial Z}{\partial y} = x^2 + g''(y) = x^2 + 3y^2$$

Comparing L.H.S & R.H.S. we get
 $g''(y) = 3y^2$, integrating we get $g(y) = y^3$

Therefore $Z(x, y) = x^2 y + y^3$

- * A differential is perfect (exact) if it derives from a function $Z(x, y)$
- * The exactness condition is $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$
- * If exact, we can find $Z(x, y)$ by integration.

WORK

If the position moves from a position x_1 to x_2

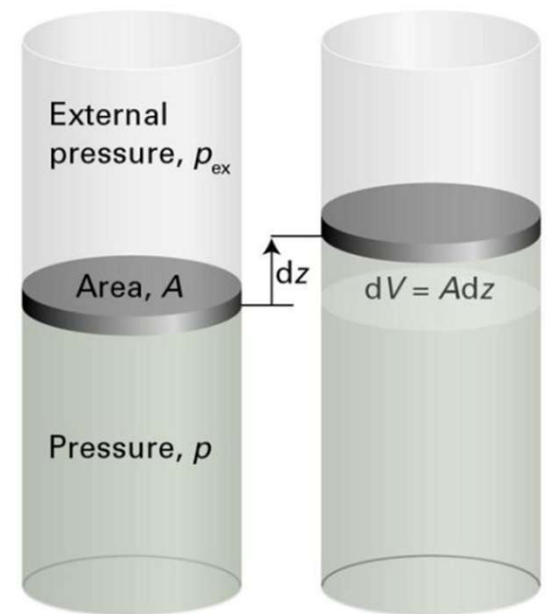
against an opposing force F , the work will be:

$$w = -\int_{x_1}^{x_2} F dx$$

The negative sign in this equation confirms to our stated convention that work done by the gas is **negative**.

The opposing pressure: $p_{ex} = \frac{F}{A}$

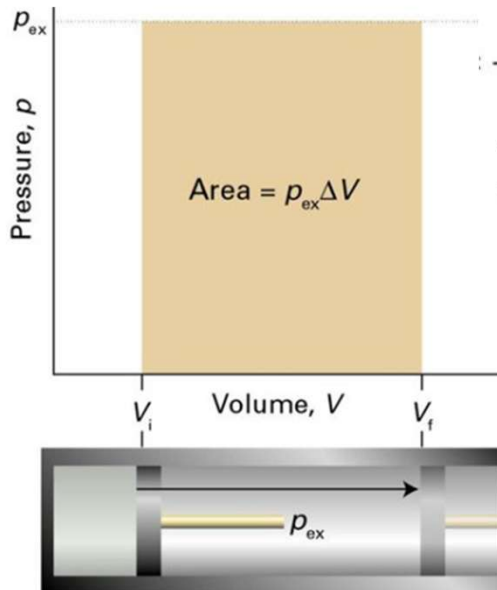
Expansion work



<http://bp.snu.ac.kr>

$$w = -\int_{x_1}^{x_2} F dx = -\int_{x_1}^{x_2} p_{ex} A dx = -\int_{V_i}^{V_f} p_{ex} dV, \text{ where } dV = A dx$$

$$-\int_{V_i}^{V_f} p_{ex} dV = -p_{ex} \int_{V_i}^{V_f} dV = -p_{ex} (V_f - V_i)$$



\therefore The work done on the system

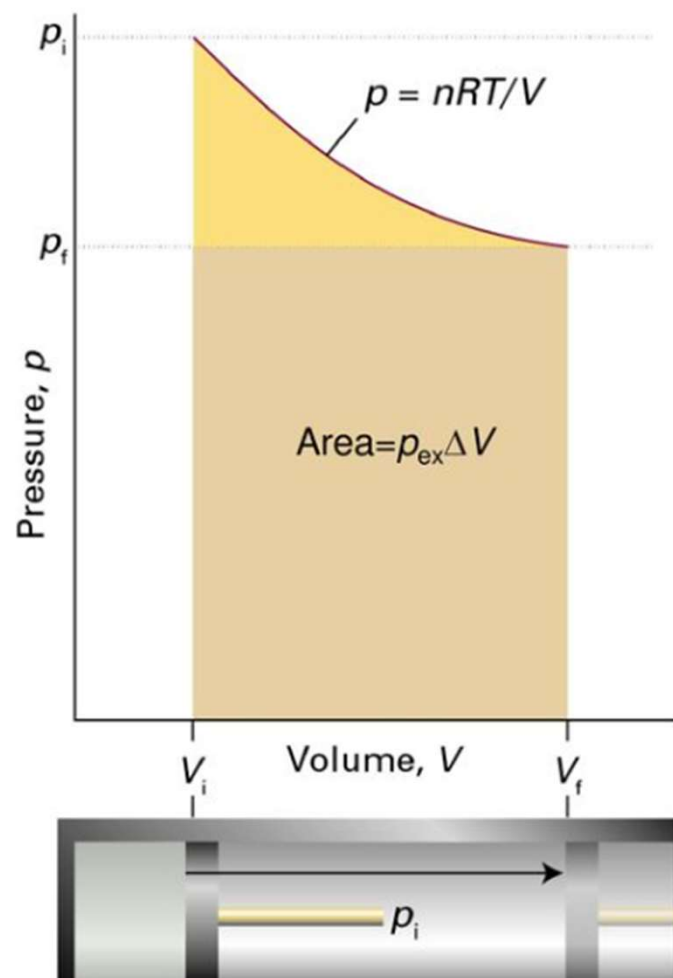
$$w = -p_{ex} \Delta V$$

When a piston of area A moves out through a distance dz , it sweeps out a volume $dV = A dz$. The external pressure, p_{ex} , is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex} A$.

Expansion, i.e., $V_f > V_i$, $w < 0$ (work done by the system on surrounding)

Compression, i.e., $V_f < V_i$, $w > 0$ (work done on the system by surrounding)

- Remember, we learned that a reversible change occurs through an infinitesimal modification of a variable



Reversible isothermal change:

$$p_{ex} \approx p_{in}$$

$$dw = -p_{ex} dV = -p_{in} dV$$

$$w = -\int_{V_i}^{V_f} p_{in} dV$$

$$pV = nRT \text{ (ideal gas)}$$

$$w = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i}$$

The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$.

The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker.

Irreversible isothermal change:

$$-\int_{V_i}^{V_f} p_{ex} dV = -p_{ex} \int_{V_i}^{V_f} dV = -p_{ex} (V_f - V_i) = -p_{ex} \Delta V$$

Conclusion:

$$|W_{rev}| > |W_{irrev}|$$

First Law of Thermodynamics

$$\Delta U = q + w$$

(1)

Process	Sign convention
Transfer of heat to the system from the surrounding	$q > 0$
Transfer of heat from the system to the surrounding	$q < 0$
Expansion of system against an external pressure	$w < 0$
Compression of system by an external pressure	$w > 0$

• For an infinitesimal change in state, $dU = \delta q + \delta w$

• For an adiabatic process $\delta q = 0 \Rightarrow dU = \delta w$

• For a cyclic process $\Delta U = \oint dU = 0 \Rightarrow q + w = 0$

If w is restricted to mechanical/pressure-volume work only $w = p dv$, then,

$$q = du + p dv \quad (2)$$

Mathematical Formulation and Implications of 1st law

Again, $U = f(T, V)$ & on differentiation,

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

Putting in eqⁿ(2), we have $q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$ — (3)

But at constant V , $q = \left(\frac{\partial U}{\partial T}\right)_V dT$

or, $\left(\frac{q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = \bar{C}_V$, molar heat capacity at constant volume

Thus, the eqⁿ(3) becomes,

$$q = \bar{C}_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad \text{--- (4)}$$

This is the generalised mathematical form of 1st law of Thermodynamics.

However, for n moles of a gas,

eqⁿ(4) becomes, $q = n\bar{C}_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$ — (5)

For ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$ & hence, $q = n\bar{C}_V dT + PdV$ — (6)

Home-work:

Prove \rightarrow For Van der Waals gas, $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ & so, $q = n\bar{C}_v dT + \left[p + \frac{an^2}{V^2}\right]dV$

Some special cases:-

- (1) Energy change in cyclic process, $dU = 0$
Eqⁿ(1) becomes, $q = w$ i.e. heat is completely converted into work.
- (2) Energy change in isothermal process & for ideal gas,
 $dU = n\bar{C}_v dT = 0$ & $q = w$
- (3) Energy change in isochoric process: $dV = 0$ & $q = dU = n\bar{C}_v dT$,
heat supplied only increases internal energy & thereby increases T .
- (4) Energy change in isolated system: $q = 0$ & eqⁿ(1) becomes
 $0 = dU + w$

For ideal gas involving mechanical work only,
 $w = PdV$ & $dU = n\bar{C}_v dT$

$$\text{hence, } P(V_2 - V_1) = -n\bar{C}_v(T_2 - T_1)$$

$$\text{or, } P(V_2 - V_1) = n\bar{C}_v(T_1 - T_2).$$

Thus, in adiabatic expansion of the gas, when $V_2 > V_1$, in order to balance $T_1 > T_2$, i.e, adiabatic expansion of an ideal gas causes fall in temp while adiabatic compression causes increase in temp.

Reversible Adiabatic Process: Relation between P, V, & T

(1) Relation between V & T: 1st Law in adiabatic process for ideal gas is, $0 = n \bar{C}_v dT + P dv$. But $P = \frac{nRT}{V}$

hence, $0 = n \bar{C}_v dT + nRT \frac{dv}{V}$

Separating the variables and integrating,

$$-\bar{C}_v \int_{T_1}^{T_2} \frac{dT}{T} = R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{or, } -\bar{C}_v \ln \frac{T_2}{T_1} = R \ln \frac{V_2}{V_1} = (\bar{C}_p - \bar{C}_v) \ln \frac{V_2}{V_1}$$

$$\text{or, } \ln \frac{T_1}{T_2} = (r-1) \ln \frac{V_2}{V_1}$$

$$\text{or, } \boxed{T_1^{r-1} V_1 = T_2^{r-1} V_2}$$

$$\text{or, } TV^{r-1} = \text{constant}$$

(4) Relation between P & V: For n moles ideal gas, $PV = nRT$

$$\text{or, } Pdv + vdp = nRdT$$

$$\text{or, } n dT = \frac{Pdv + vdp}{R}$$

Putting this in the 1st Law, $0 = \bar{C}_v \left(\frac{Pdv + vdp}{R} \right) + Pdv$

Separating the variables & integrating

$$\text{we get, } Pdv \left(\frac{\bar{C}_v}{R} + 1 \right) = - \frac{\bar{C}_v}{R} vdp$$

$$\text{or, } \left(\frac{\bar{C}_p}{\bar{C}_v} \right) \int_{V_1}^{V_2} \frac{dv}{v} = - \int_{P_1}^{P_2} \frac{dp}{P}$$

$$\text{or, } \gamma \ln \frac{V_2}{V_1} = \ln \frac{P_1}{P_2}$$

$$\text{or, } \boxed{P_1 V_1^\gamma = P_2 V_2^\gamma}$$

$$\text{or, } PV^\gamma = \text{constant}$$

(3) Relation between T & P :-

We have, $PdV = nRdT - VdP$ & this on putting in the 1st law,

We have, $0 = n\bar{C}_v dT + nRdT - VdP$

$$\text{or, } VdP = n(\bar{C}_v + R)dT$$

But $V = nR\frac{T}{P}$, hence, $nR\frac{T}{P}\frac{dP}{P} = n\bar{C}_p dT$

$$\text{or, } \frac{R}{\bar{C}_p} \int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\text{or, } \left(1 - \frac{\bar{C}_v}{\bar{C}_p}\right) \ln \frac{P_2}{P_1} = \ln \frac{T_2}{T_1}$$

$$\text{or, } \left(\frac{1-\gamma}{\gamma}\right) \ln \frac{P_2}{P_1} = \ln \frac{T_1}{T_2}$$

$$\text{or, } (1-\gamma) \ln \frac{P_2}{P_1} = \gamma \ln \frac{T_1}{T_2}$$

$$\text{or } \boxed{\frac{\gamma}{T_1} \frac{1-\gamma}{P_1} = \frac{\gamma}{T_2} \frac{1-\gamma}{P_2}}$$

$$\text{or, } \frac{\gamma}{T_1} \frac{1-\gamma}{P_1} = \text{Constant}$$

$$dU = \delta q + \delta w, \delta q = 0 \Rightarrow \delta w = dU = n C_V dT$$

$$w = - \int_1^2 p_{ext} dV = n C_V (T_2 - T_1)$$

- Reversible adiabatic expansion: Obtain T2, using any of the following:
 $TV^{\gamma-1} = \text{const}; T^{\gamma}P^{1-\gamma} = \text{const}$

Workdone: $W_{rev} = \frac{P_1 v_1 - P_2 v_2}{\gamma - 1}$

- Irreversible adiabatic expansion against a constant pressure, $P_{ext} = P_2$
 Obtain T2 as follows : $nC_V dT = -P_2 dv = -P_2(v_2 - v_1) = -P_2 \left(\frac{nRT_2'}{P_2} - \frac{nRT_1}{P_1} \right)$

Workdone, $w_{irrev} = P_2(v_2 - v_1)$

Adiabatic Expansion (Work Done BY the Gas)

- The gas **expands**, increasing its volume ($V_2 > V_1$).
- Since **pressure and temperature drop**, the gas does **positive work on the surroundings**.
- The work done is **extracted as useful energy** in turbines, engines, and rocket nozzles.

•**Example:** In power plants (thermal, nuclear, or geothermal), high-pressure steam or gas expands adiabatically through a turbine. The expanding steam pushes turbine blades, converting thermal energy into mechanical work. This mechanical work is then used to drive generators, producing electricity.

❑ Diesel Engine (Adiabatic Compression & Expansion) 🚗

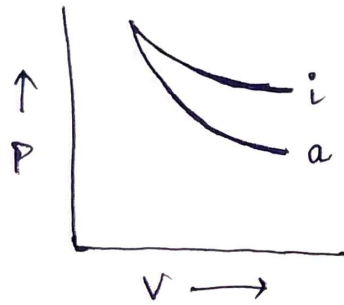
How It Works: In a diesel engine, air is adiabatically compressed inside the cylinder. Compression increases temperature, igniting fuel without a spark. The expanding gases push the piston, performing work.

- ◆ Why Adiabatic? The compression is so rapid that no heat is lost to the surroundings. The expansion stroke does useful work by moving the piston.

- ◆ Examples: Trucks, ships, and heavy machinery use diesel engines. Some high-efficiency gasoline engines use similar principles.

More applications: In Space Propulsion, Adiabatic Cooling in Atmospheric Science & Refrigeration.

To show that adiabatic curve is steeper than isothermal in P-V diagram



To show that adiabatic slope > isothermal slope

$$\text{i.e.} \rightarrow \left(\frac{dp}{dv}\right)_a > \left(\frac{dp}{dv}\right)_i$$

For isothermal process involving ideal gas,

$$PV = \text{Constant},$$

$$\text{or, } Pdv + vdp = 0$$

$$\text{or, } \left(\frac{dp}{dv}\right)_i = -\left(\frac{P}{V}\right) \text{ --- (A)}$$

For adiabatic process of ideal gas, $PV^\gamma = \text{Constant (C)}$

$$\text{or, } \ln P + \gamma \ln V = \ln C$$

$$\text{or, } \frac{1}{P} \cdot dp + \frac{\gamma}{V} \cdot dV = 0$$

$$\text{or, } \left(\frac{dp}{dv}\right)_a = -\gamma \left(\frac{P}{V}\right) \text{ --- (B)}$$

Dividing by (A), we have

$$\frac{\left(\frac{dp}{dv}\right)_a}{\left(\frac{dp}{dv}\right)_i} = \gamma > 1$$

$$\text{Since } \gamma = \frac{\bar{C}_p}{\bar{C}_v} \text{ \& } \bar{C}_p > \bar{C}_v$$

$$\text{Hence, } \left(\frac{dp}{dv}\right)_a > \left(\frac{dp}{dv}\right)_i$$

That is,
adiabatic curve is steeper than isothermal in P-V diagram.