Lecture 13: Laws of Thermodynamics, PV Diagrams

Reversibility, Zero and First Law, PV Diagrams

Reversibility

Reversible

- Idealized process
- Occurs slowly with infinitesimal small steps
- Keywords: infinitesimally slow, gradually, maintaining equilibrium, ideal: "frictionless piston"

Irreversible

- Non-ideal, Real world process
- Occurs quickly, real time scale
- Loss of efficiency due to heat loss, friction, inefficiencies
- Some idealized processes can be irreversible - mixing

Laws of Thermodynamics

Zeroth Law

If two systems A and B are in thermal equilibrium with C, then they are in thermal equilibrium with each other, no heat will flow.

First Law

$$\Delta U = q + w \qquad dU = dq + dw$$

Temperature, Internal Energy, and Heat

- Temperature is a measure of average kinetic energy, not internal energy
- Change in internal energy is related to T (isothermal processes)
- Temperature is related to heat, but adding heat does not mean T changes (heat is energy transfer)

Evaluating State vs Path Functions

State Function

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

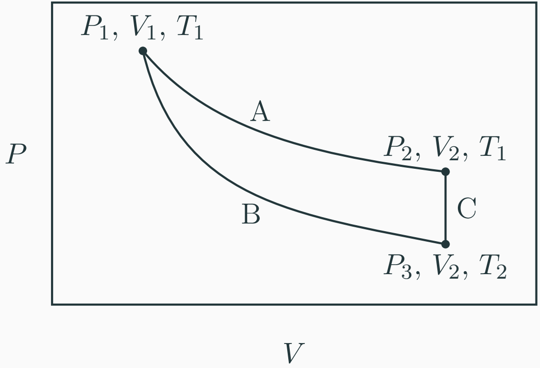
For a cycle, change in internal energy is always zero as return to same reference

Path Function

$$\int_1^2 dw = w \quad (\text{not } w_2 - w_1)$$

For a cycle, work and heat are non-zero as these are path dependant quantities

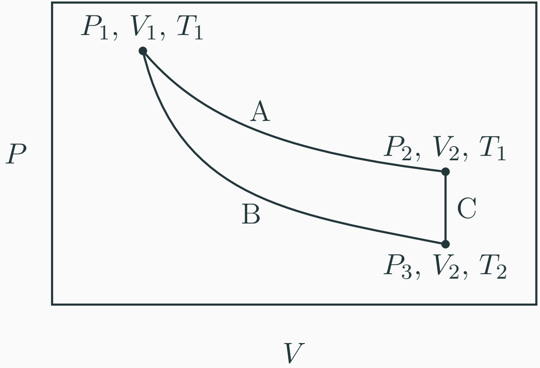
PV Diagrams (Reversible)



A: Isothermal Expansion
Isothermal, constant T

$$\Delta U = 0$$
$$q = -w$$
$$w = -nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

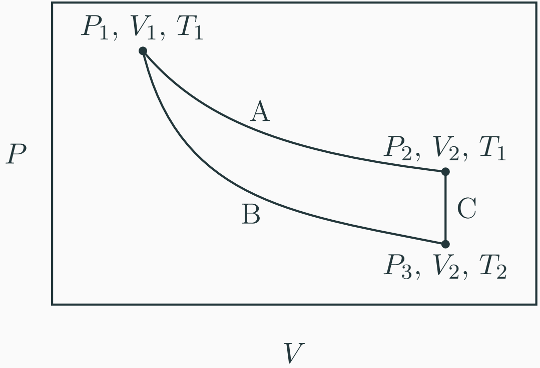
PV Diagrams (Reversible)



B: Adiabatic Expansion

- Gas is expanding
- Work is done BY the gas
- No heat, so internal energy decreases
- Temperature decreases

PV Diagrams (Reversible)



B: Adiabatic Expansion

Definitions:

$$dU = dq + dw \qquad dq = 0$$

Combine:

$$dU = dw$$

U only depends on T:

$$dU = C_V(T)dT \implies C_V = \frac{dU}{dT}$$

Adiabatic Expansion of Monoatomic Ideal Gas

$$dU = C_V\,dT = dw = -P\,dV$$

Substitute in $\overline{C_V} = \frac{3}{2}R$ and $PV = nRT$:

$$\frac{3}{2}nR\,dT = -P\,dV = -\frac{nRT}{V}\,dV$$

Group similar terms and integrate:

$$\frac{3}{2}\int_{T_1}^{T_2}\frac{1}{T}\,dT = -\int_{V_1}^{V_2}\frac{1}{V}\,dV$$

Evaluate at bounds:

$$\frac{3}{2}\ln\left(\frac{T_2}{T_1}\right) = -\ln\left(\frac{V_2}{V_1}\right)$$

$$\implies \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{2/3}$$

Adiabatic Expansion of Monoatomic Ideal Gas

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{2/3}$$

Substitute into ideal gas law:

$$PV = nRT$$

$$\frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{2/3}$$

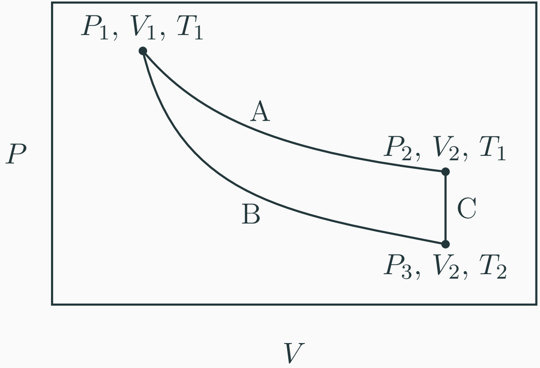
Rearrange and simplify:

$$P_1 V_1^{5/3} = P_2 V_2^{5/3}$$

Adiabatic Relation

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

PV Diagrams (Reversible)



B: Adiabatic Expansion

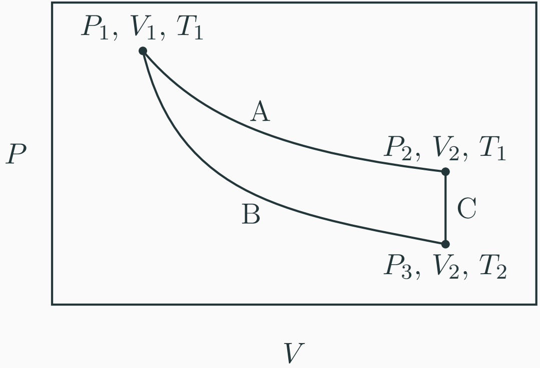
Adiabatic, $q = 0$

$$\Delta U = w$$

$$q = 0$$

$$w = \int_{T_1}^{T_2} C_V dT$$

PV Diagrams (Reversible)

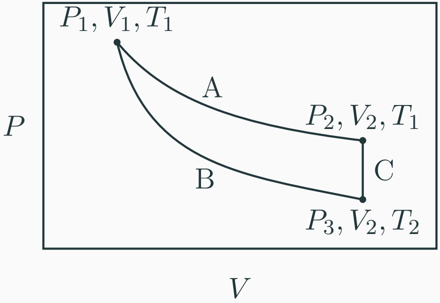


C: Isochoric Heating

Isochoric, constant V

$$\Delta U = q$$
$$q = \int_{T_2}^{T_1} C_V dT$$
$$w = 0$$

PV Diagrams: State vs Path



Process	ΔU	w	q
Isothermal	0	$-nRT_1 \ln\left(\dfrac{V_2}{V_1}\right)$	$-w$
Adiabatic	w	$\displaystyle\int_{T_1}^{T_2} C_V \, dT$	0
Isochoric	q	0	$\displaystyle\int_{T_2}^{T_1} C_V \, dT$