FIRST LAW OF THERMODYNAMICS

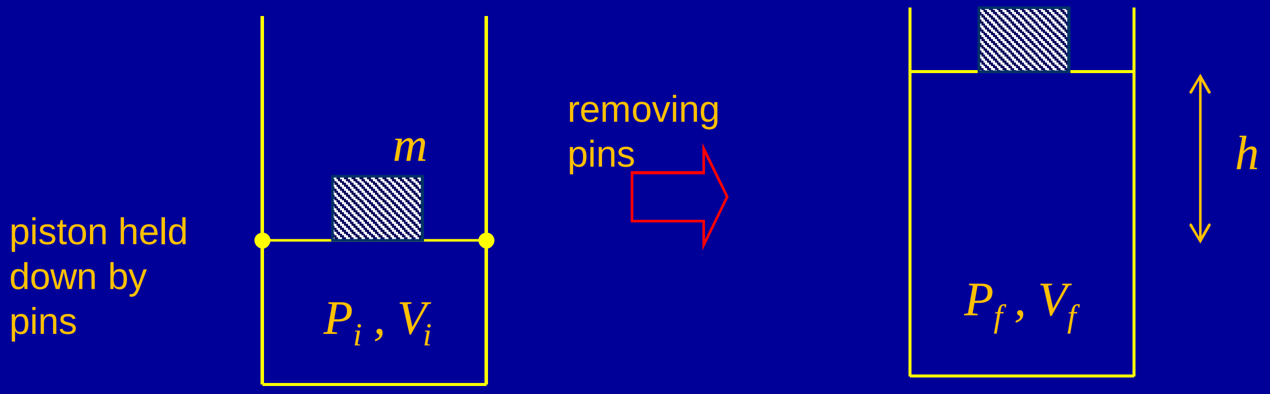
Reversible Processes

Free Expansion

Mechanical Work

Mechanical Work

Expansion of a gas



Work performed by the gas: $\boxed{w = -P_{\text{ext}}\Delta V}$

Infinitesimal volume change: $\boxed{\delta w = -P_{\text{ext}}\delta V}$

Convention: work done on the system is taken as positive.

$$\boxed{w = -\int_{V_i}^{V_f} P_{\text{ext}}(V)\,dV}$$

Reversible Processes

A process is called reversible if $P_{system} = P_{ext}$ at all times. The work expended to compress a gas along a reversible path can be completely recovered upon reversing the path.

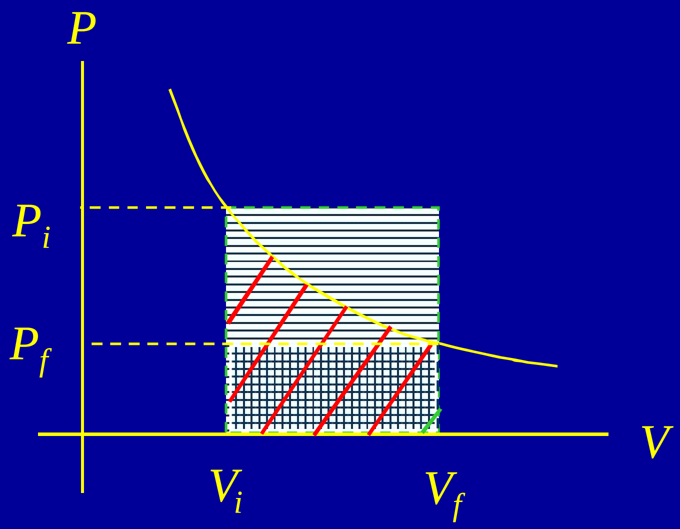
When the process is reversible the path can be reversed, so expansion and compression correspond to the same amount of work.

$$w = -\int_{V_i}^{V_f} P(V)dV$$

- ❖ To be reversible, a process must be infinitely slow.

Reversible Isothermal Expansion/Compression of Ideal Gas

P



$$w = -nRT \ln \frac{V_f}{V_i}$$

Reversible isothermal compression: minimum possible work

Reversible isothermal expansion: maximum possible work

Exact and Inexact Differentials

A state function is a property that depends solely on the state of the system. It does not depend on how the system was brought to that state.

When a system is brought from an initial to a final state, the change in a state function is independent of the path followed.

An infinitesimal change of a state function is an exact differential.

$$\text{Internal energy } U\text{: state function}$$

$$dU\text{: exact differential}$$

$$\int dU = U_f - U_i = \Delta U\text{; independent of the path}$$

Work and heat are not state functions and do not correspond to exact differentials.

Of the three thermodynamic variables, only two are independent. It is convenient to choose V and T as the independent variables for U.

The First Law

P The sum of the heat *q* transferred to a system and the work *w* performed on it equal the change D*U* in the system’s internal energy.

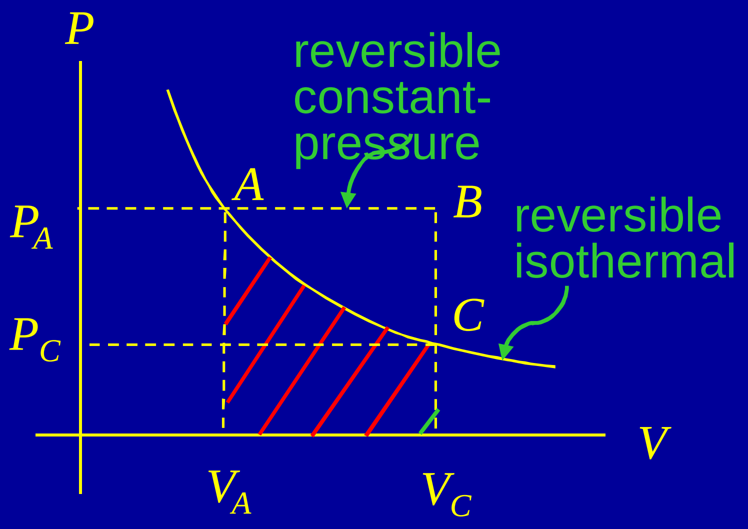
$$\Delta U = q + w$$

Postulate: The internal energy is a state function of the system.

Work and heat are not state functions and do not correspond to exact differentials.

$$dU = \text{đ}q - PdV$$

Work and Heat along Reversible Isothermal Expansion for an Ideal Gas, where U=U(T)



$$T_B = T_A \frac{V_C}{V_A}$$

$$w_{AC} = -nRT_A \ln \frac{V_C}{V_A}$$

$$w_{BC} = 0$$

$$w_{AB} = -P_A\left(V_B - V_A\right)$$

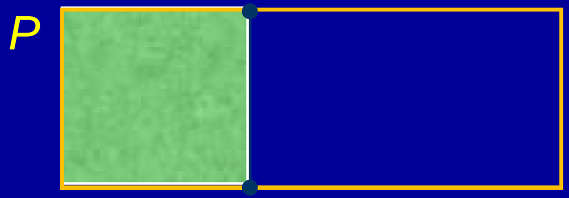
$$\Delta U_{AC} = 0 \Longrightarrow q_{AC} = nRT_A \ln \frac{V_C}{V_A}$$

$$q_{BC} = \Delta U_{BC} = \int_{T_B}^{T_C} c_V\, dT$$

$$\Delta U_{AB} = \int_{T_A}^{T_B} c_V\, dT$$

$$q_{AB} = \Delta U_{AB} - w_{AB} = \int_{T_A}^{T_B} c_V\, dT + P_A\left(V_B - V_A\right)$$

Free Expansion



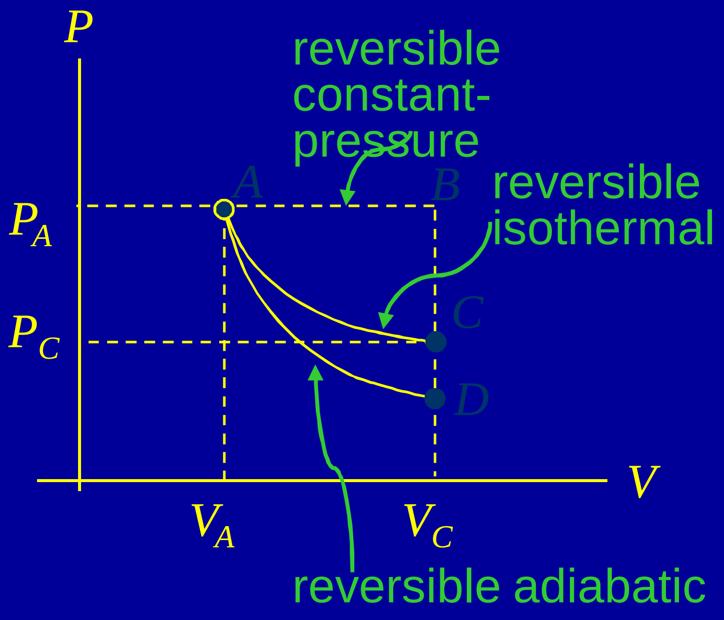
Suddenly remove the partition

No work, no heat! $\Delta U = 0$

$$dU = c_V\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad U = U(T) \Leftrightarrow \Delta T = 0$$

For real, non-ideal gases these hold approximately, and $\left(\frac{\partial U}{\partial V}\right)_T$ is small.

A process is called adiabatic if no heat is transferred to or out of the system.



$$\Delta U = w_{\text{ad}}, \quad dU = dw_{\text{ad}}$$

$$dU = c_V\,dT = -P\,dV$$

$$P \quad = -\frac{nRT}{V}\,dV \quad \text{(ideal gas)}$$

If $c_V(T)$ is known, this can be used to determine T (and thus also P) as a function of V.

For a monatomic ideal gas,

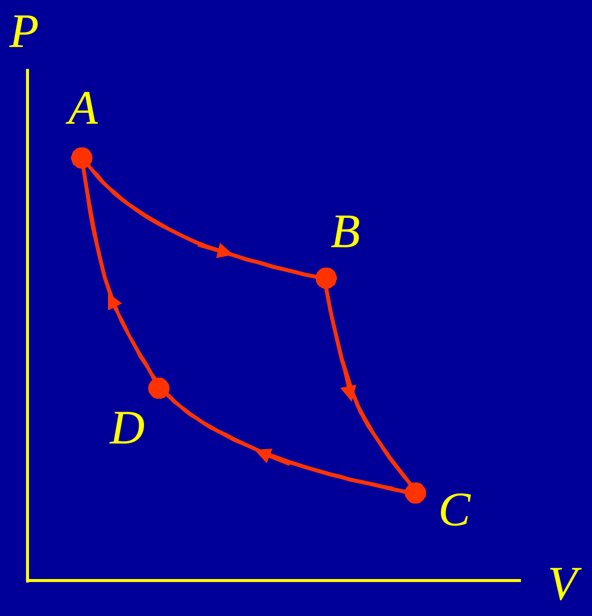
$c_V = \frac{3}{2} nR$ independent of $T \Rightarrow$

$$\left(\frac{T_D}{T_A}\right)^{\frac{3}{2}} = \frac{V_A}{V_D}$$

Adiabatic cooling!

Gases heat up when compressed adiabatically.
(This is why the pump used to inflate a tire becomes hot during pumping.)

The Carnot Cycle



AB: reversible isothermal at temperature T_1

BC: reversible adiabatic

CD: reversible isothermal at temperature $T_2 < T_1$

DA: reversible adiabatic

$$\Delta U_{ABCDA} = 0 \Longrightarrow q_{AB} + q_{CD} = -w > 0$$

(the system does work)

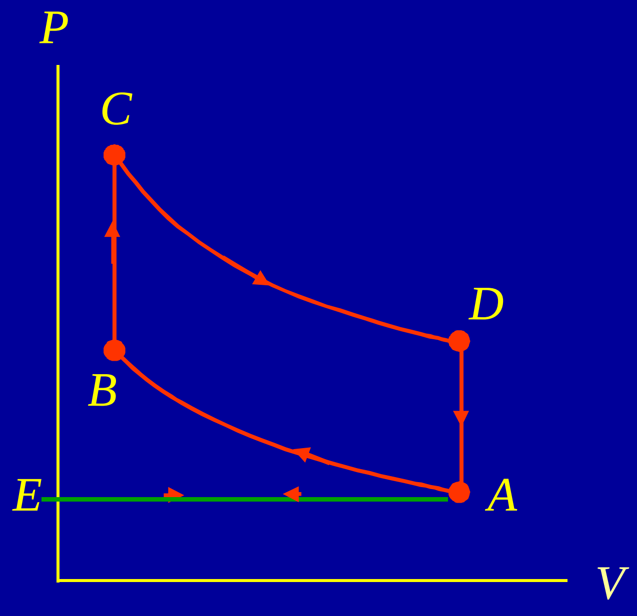
Efficiency of Carnot engine:

$$\eta = \frac{|w|}{q_{AB}} = 1 - \frac{|q_{CD}|}{q_{AB}}$$

$$\eta = 1 - \frac{T_2}{T_1} < 1 \quad (\text{unless} \;\; T_2 = 0)$$

One can never utilize all the thermal energy given to the engine by converting it into mechanical work.

Thermodynamics of the Otto Cycle



Reversible adiabatic compression AB: $T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1}$

BC is reversible absorption of heat q_h from a series of reservoirs whose temperatures range from T_B to T_C:

$$q_h = \int_{T_B}^{T_C} c_V \, dT.$$

If we assume c_V is constant, $q_h = c_V(T_C - T_B)$.

Reversible adiabatic expansion CD: $T_C V_C^{\gamma-1} = T_D V_D^{\gamma-1}$ or $T_C V_B^{\gamma-1} = T_D V_A^{\gamma-1}$

DA is reversible rejection of heat q_c to a series of reservoirs whose temperatures range from T_D to T_A: $q_c = \int_{T_D}^{T_A} c_V \, dT = c_V(T_A - T_D)$

$$\eta = 1 - \frac{|q_c|}{q_h} = 1 - \frac{T_D - T_A}{T_C - T_B} = 1 - \left(\frac{V_B}{V_A}\right)^{\gamma-1}$$

V_B / V_A : compression ratio