

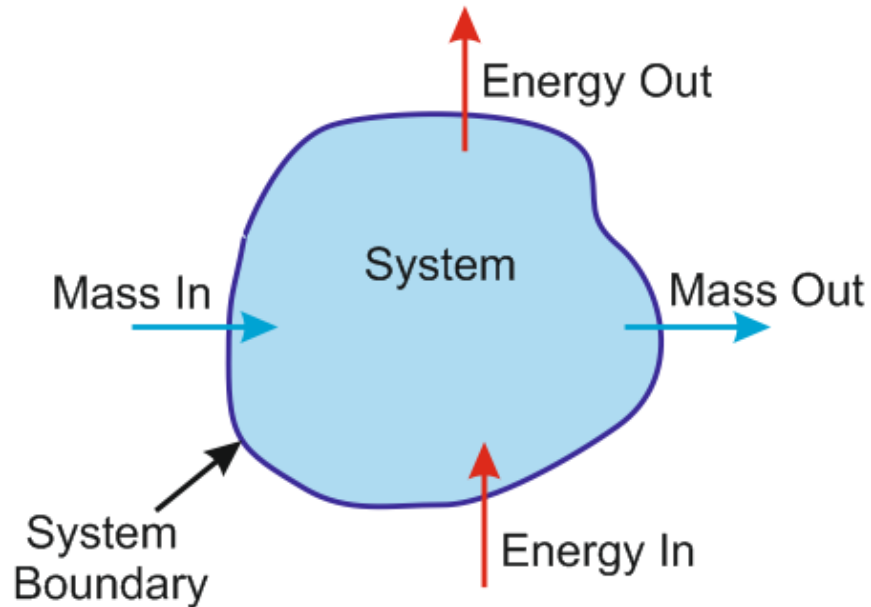
Lecture 2

Temperature, Energy, Heat and Work
First principle of thermodynamics

22.08.2018

Thermodynamic system

What kind of energy is exchanged?!



- **Open:** Mass and Energy can transfer between the System and the Surrounding
- **Closed:** Energy can transfer between the System and the Surroundings, but NOT mass
- **Isolated:** Neither Mass nor Energy can transfer between the System and the Surroundings

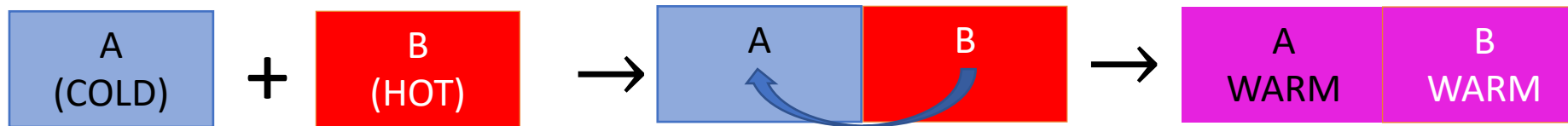
The state of a thermodynamic system



Some properties (e.g. P , T) are well-defined only when the system at **equilibrium**

Thermal Equilibrium (when heat stops flowing)

- Heat flows from the **warmer** to the **cooler** object until they are in **thermal equilibrium** (no heat flow).
- In thermal equilibrium, both bodies have the same **temperature**

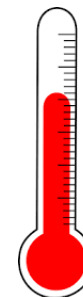


ZERO'th LAW of Thermodynamics

If A and B are in thermal equilibrium, and B and C are in thermal equilibrium, then A and C are thermal equilibrium

Consequence:

B is a thermometer measure the temperature



Celsius (°C)
Fahrenheit (°F)
Kelvin (K)

What is Temperature?

The thing we measure with a **thermometer**

- Operational definition of temperature T requires:
 - ✓ Measuring object: mercury, alcohol, platinum, semiconductors (thermistor), liquid He, gas



What is Temperature?

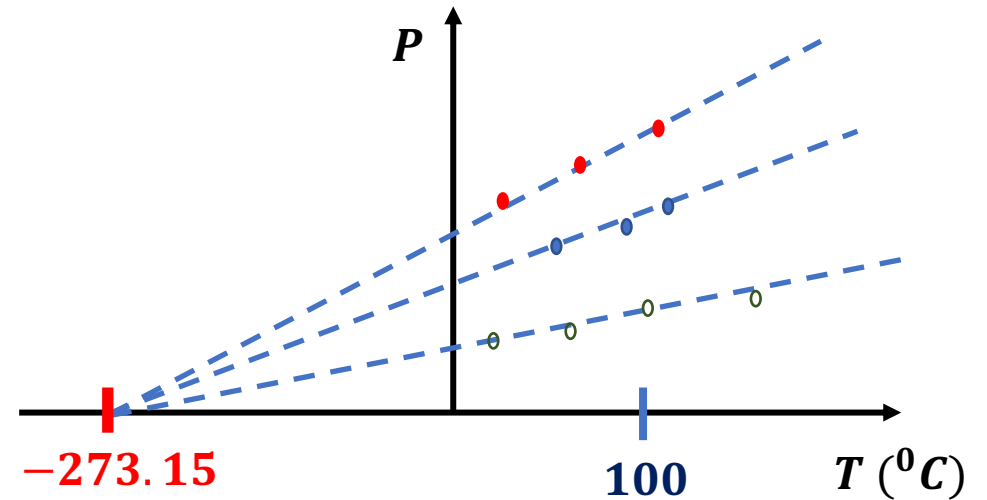
The thing we measure with a **thermometer**

- Operational definition of temperature T requires:
 - ✓ property that depends on T : *pressure, electrical resistance*
 $P(T) = \text{const.} \times T$
 - ✓ reference point: *const* fixed by the boiling point of H_2O
(calibration)
 - ✓ interpolation scheme between reference points

Gas thermometer

$$P(T) = \frac{P_{\text{boiling } H_2O}}{T_{\text{boiling } H_2O}} \times T$$

- $T_{\text{boiling } H_2O} = 373,15 \text{ K}$



- *Absolute ZERO: Kelvin scale*

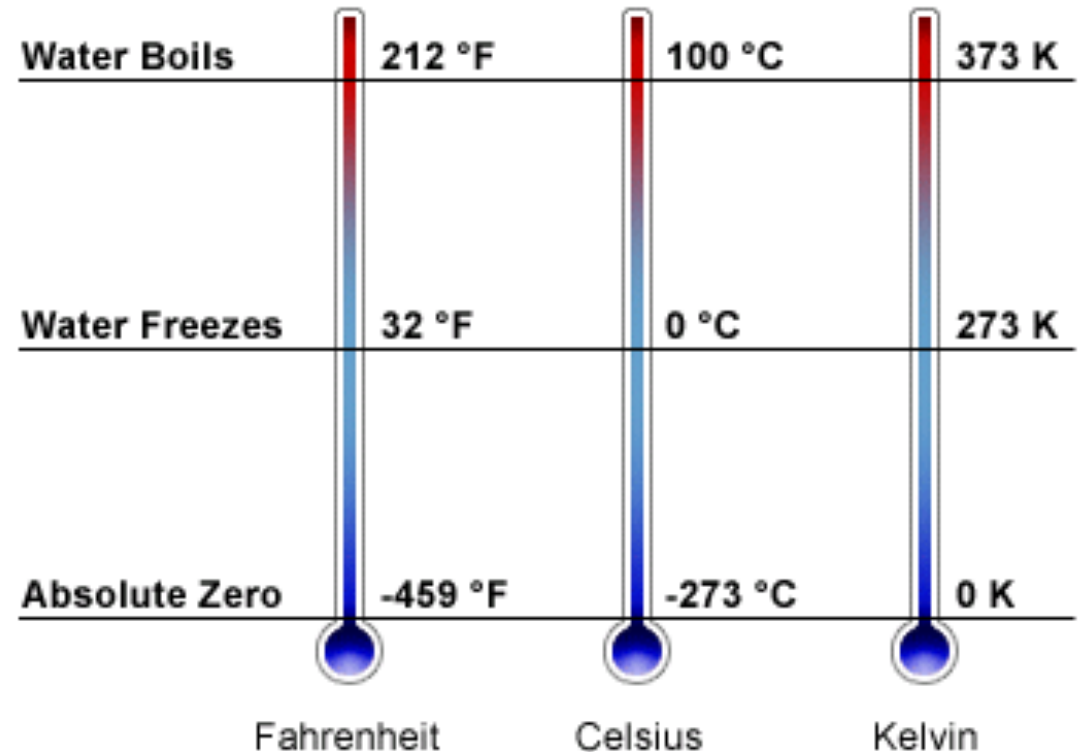
$$T_K = 0K, \quad T_C = -273.15^\circ C$$

Conversion between temperature scales

$$T_C = T_K - 273.15$$

$$T_C = (T_F - 32) \times \frac{5}{9}$$

$$T_F = T_K \times \frac{9}{5} - 459.67$$



Heat «Q»

«Thermal energy in transit»

- heat flows spontaneously from hot to cold
- Sometime heat flows in the opposite direction – refrigerator
- Heat can flow in and out of a system, but a system cannot «contain a certain quantity of heat»

NOT A STATE VARIABLE, PROCESS VARIABLE

Heat «Q»

«Thermal energy in transit»



Example:

A 1kW electric heater is switched on for 1 minute. How much heat does it produce?

Heat Capacity

How much heat is needed to raise the T of an object by a small amount dT ?

$$C \equiv \frac{dQ}{dT}, \quad [C] = 1 \text{ J K}^{-1}$$

Specific heat capacity: *Heat capacity per unit mass, or per unit (molar) volume*

$$c \equiv \frac{1}{m} \frac{dQ}{dT}, \quad [c] = 1 \text{ J K}^{-1} \text{ kg}^{-1}$$

Example: Heat Capacity of water

The heat capacity of 0.125 kg of water is measured to 523 J K^{-1} at room temperature. What is the mass-specific heat of water?

$$c = \frac{523 \text{ J K}^{-1}}{0.125 \text{ kg}} = 4.184 \times 10^3 \text{ J K}^{-1} \text{ kg}^{-1}$$

The energy to raise 1 gram of water by 1 degree is 4.184 Joules

Example: Heat Capacity of water

The heat capacity of 0.125 kg of water is measured to 523 J K^{-1} at room temperature. What is the mass-specific heat of water?

$$1 \text{ Calorie} = 4.184 \text{ J}$$

A protein bar (100g) can contain about 414 Calories, which is equal to the heat required to raise the temperature of 100 g (0.1 liter) water by 1 degree.

The heat to raise 100 g of Cu by one degree is

$$38,5 \text{ J} = 9,2 \text{ Cal} \approx .02 \text{ protein bar}$$

Heat Capacity depends on circumstances

How much heat is needed to raise the T of an object by a small amount dT by keeping the volume constant?

$$C_V \equiv \left(\frac{\partial Q}{\partial T} \right)_V, \quad [C_V] = 1 \text{ J K}^{-1}$$

Specific heat capacity at constant volume: *Isocoric heat capacity per unit mass, or per unit (molar) volume*

$$c_V \equiv \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right)_V, \quad [c_V] = 1 \text{ J K}^{-1} \text{ kg}^{-1}$$

Heat Capacity under constraint

How much heat is needed to raise the T of an object by a small amount dT by keeping the pressure constant?

$$C_P \equiv \left(\frac{\partial Q}{\partial T} \right)_P, \quad [C_P] = 1 \text{ J K}^{-1}$$

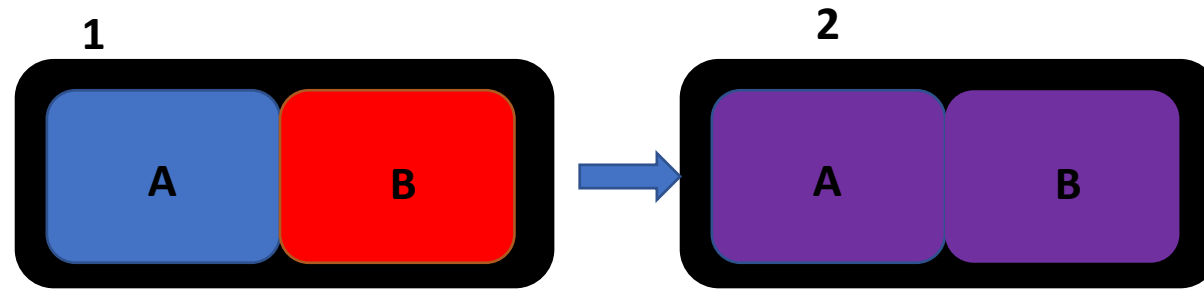
Specific heat capacity at constant pressure: *Isobaric heat capacity per unit mass, or per unit (molar) volume*

$$c_P \equiv \frac{1}{m} \left(\frac{\partial Q}{\partial T} \right)_P, \quad [c_P] = 1 \text{ J K}^{-1} \text{ kg}^{-1}$$

- specific heat capacity of water at constant pressure at 15°C*

$$c_P = 4.184 \times 10^3 \text{ J K}^{-1} \text{ kg}^{-1}$$

Relaxation
to thermal
equilibrium



What is the final temperature at thermal equilibrium?

A: no net heat exchange of the whole system with its environment (isolated system)

$$\delta Q_A = -\delta Q_B \rightarrow C_V dT_A = -C_V dT_B$$

$$T = \frac{T_A + T_B}{2}$$

Work «W»

Another form of «energy in transit»

Mechanical work: exchange of energy resulting in volume expansion or contraction due to pressure

Chemical work: exchange of energy due to particles entering or leaving the system

Magnetic work: exchange of energy between the system and its surrounding resulting in a net magnetization

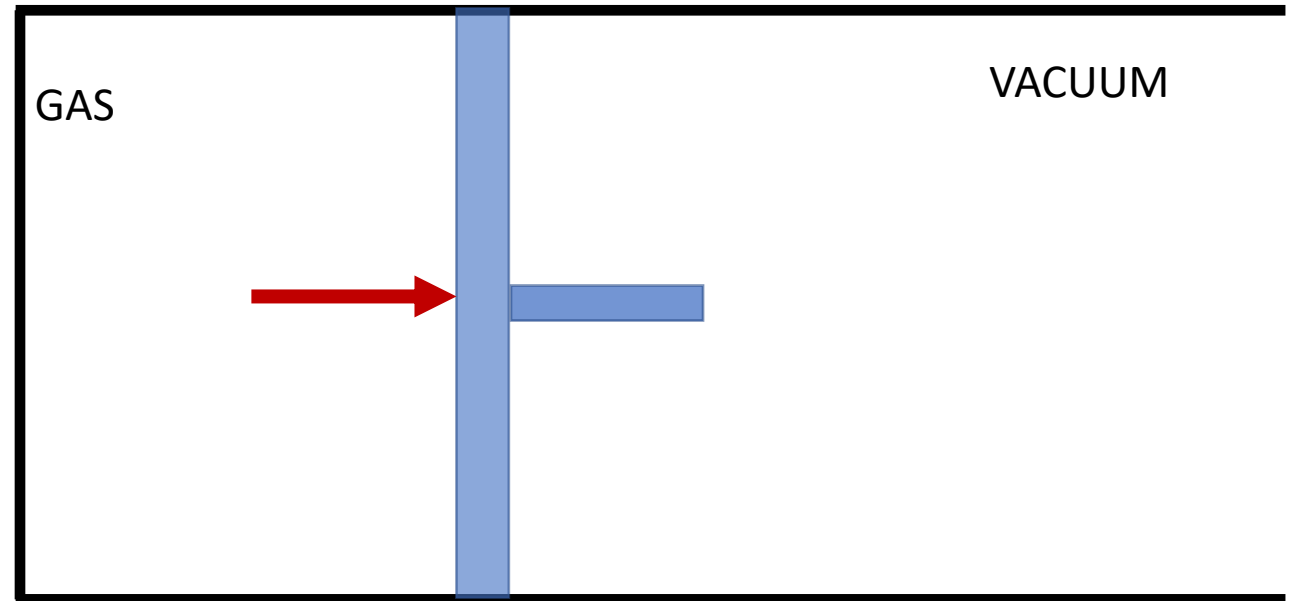
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$$[W] = 1 J$$

Free Gas Expansion

NATURAL IRREVERSIBLE EXPANSION

What changes during this expansion?



Work: REVERSIBLE Gas contraction

IMAGINE A REVERSIBLE PATH

$$\vec{F} = -PA \vec{n}$$

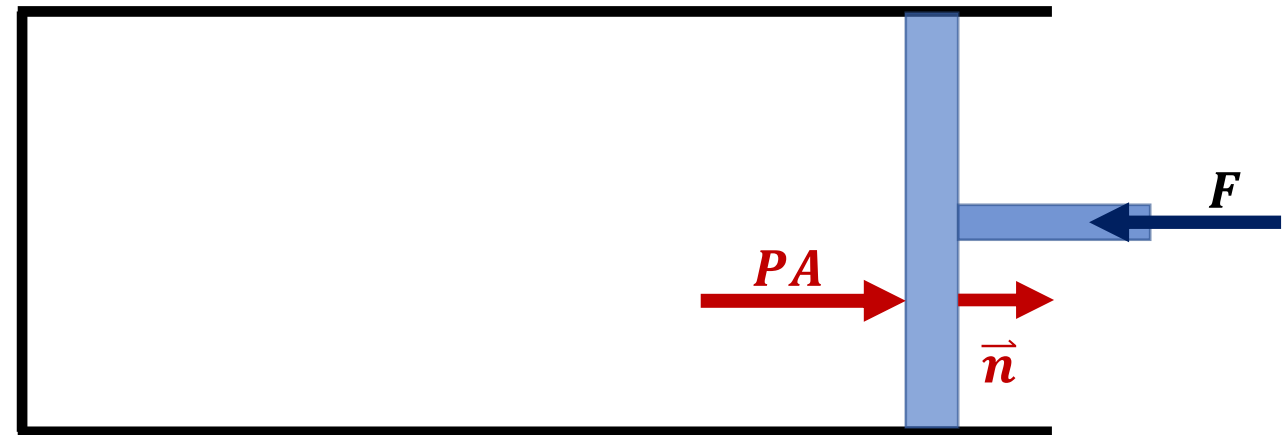
$$\delta W_{ext} = \vec{F} \cdot \overrightarrow{dx}$$

$$\delta W_{ext} = -PA \vec{n} \cdot \overrightarrow{dx}$$

Total work done by *the gas*

$$W = - \int_{V_1}^{V_2} P dV$$

(sign convention: $W < 0$ when the gas does work
hence it loses some of its energy)



$W > 0$ compression

$W < 0$ expansion

Isothermal Gas expansion

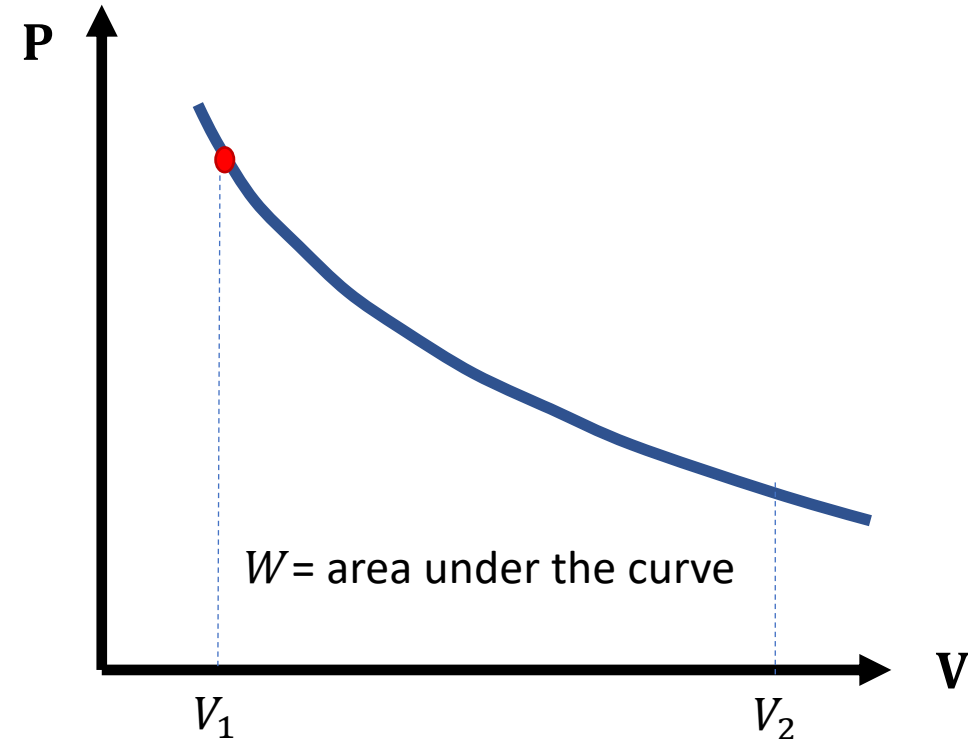
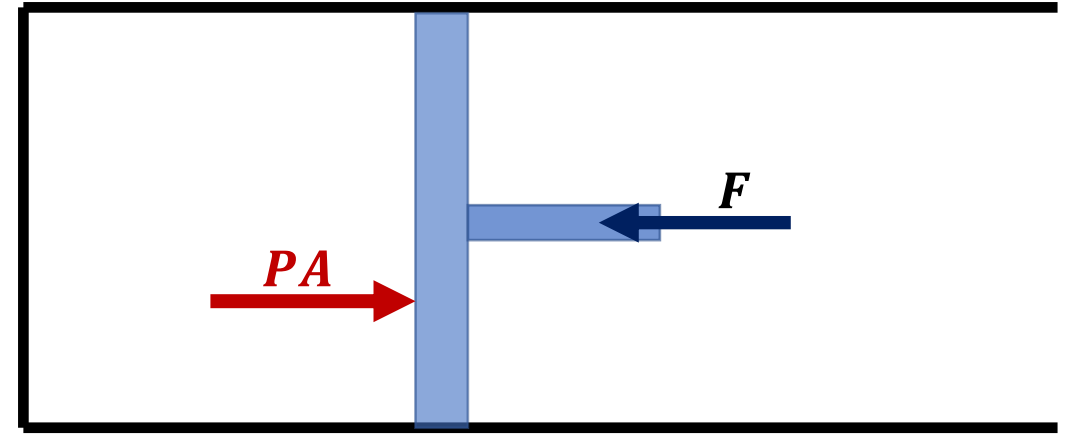
$$W = - \int_{V_1}^{V_2} P dV$$

Ideal gas: $PV = nRT$

1. Isothermal path

$$W = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$W = -nRT \ln \frac{V_2}{V_1}$$



Isocoric «gas expansion»

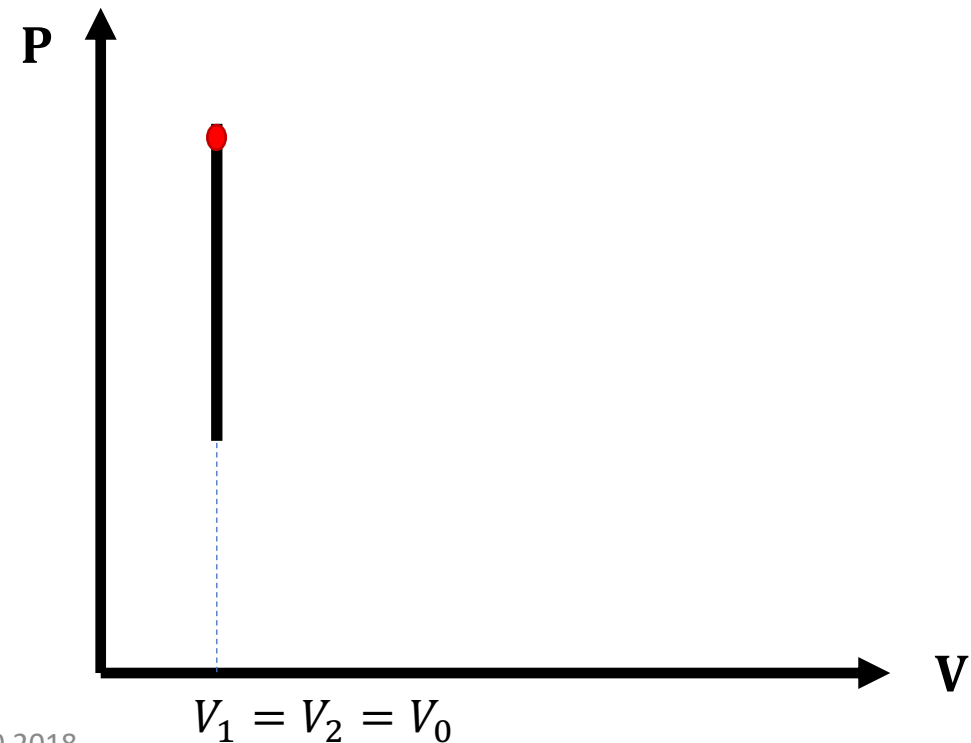
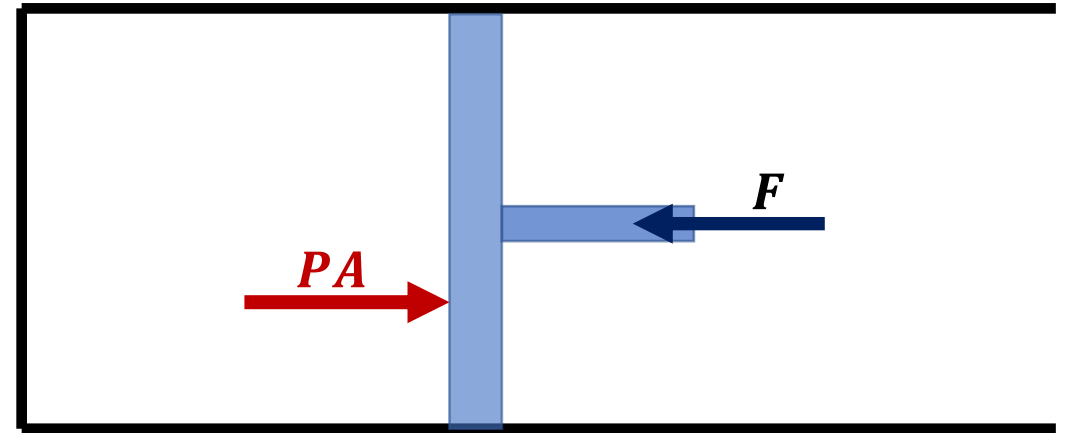
$$W = - \int_{V_1}^{V_2} P dV$$

2. Isocoric path

$$V = V_0$$

$$W = - \int_{V_0}^{V_0} P dV$$

$$W = 0$$



Isobaric gas expansion

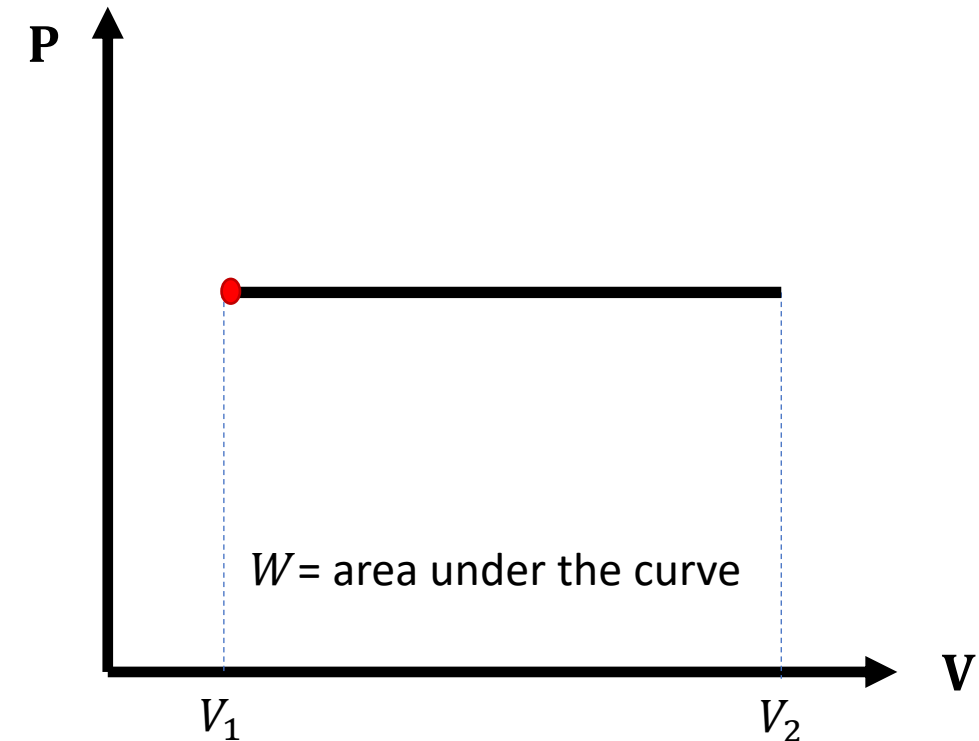
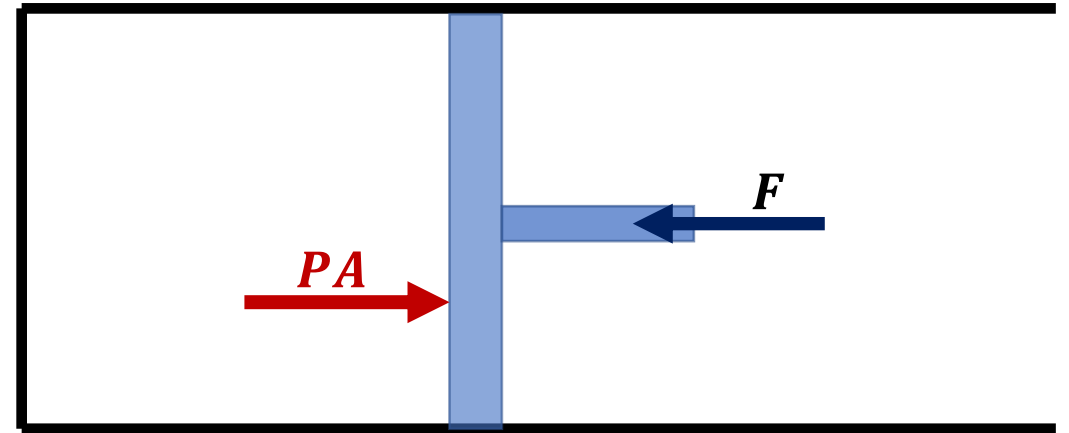
$$W = - \int_{V_1}^{V_2} P dV$$

3. Isobaric path

$$P = P_0$$

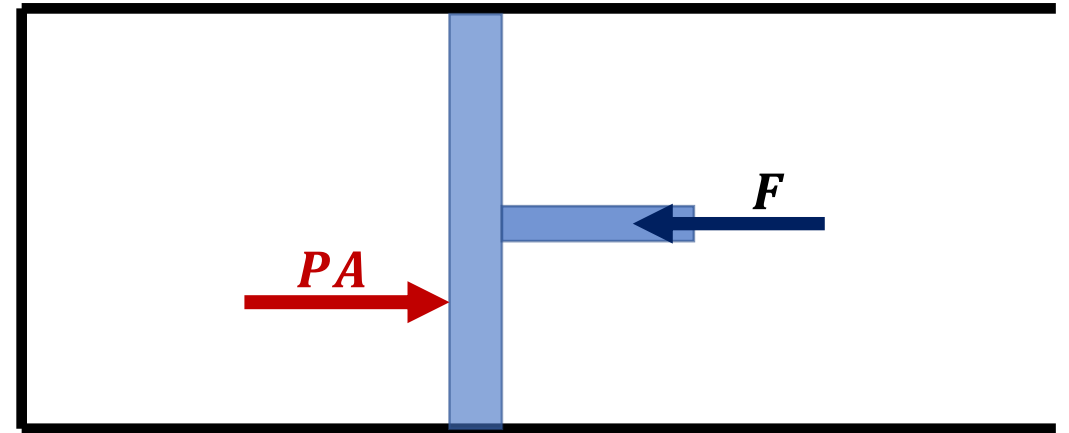
$$W = -P_0 \int_{V_1}^{V_2} dV$$

$$W = -P_0 (V_2 - V_1)$$



1. Isothermal path

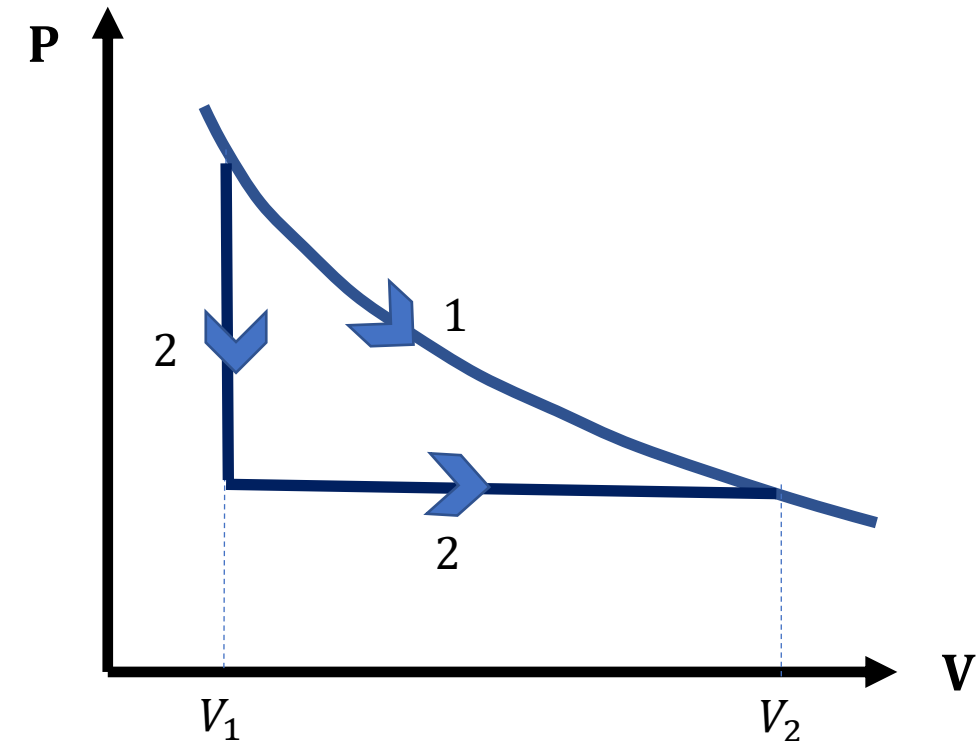
$$W = -nRT \ln \frac{V_2}{V_1}$$



2. Isocoric + Isobaric path

$$W = -P_0 (V_2 - V_1)$$

WORK IS PATH-DEPENDENT



First law of thermodynamics

Conservation of energy

The total change in the internal energy of a system is the sum of heat and work exchanges with the surrounding

$$\Delta U = W + Q$$

The change in the «stored» energy equal the sum of «energies in transit»

The infinitesimal change in energy

$$dU = \delta W + \delta Q$$

Isocoric process: no work

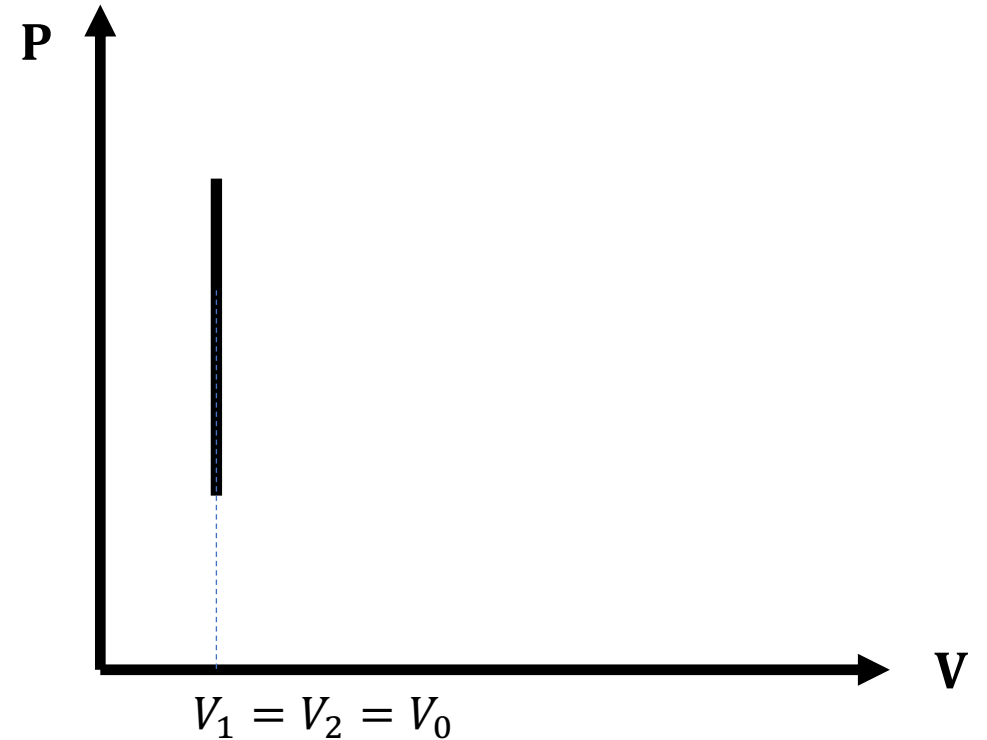
$$dU = -PdV + \delta Q \rightarrow dU = \delta Q$$

«Energy capacity»

- $C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \frac{dU}{dT}$

Energy needed to raise T by one degree

- $dU = C_V dT \rightarrow U = U(T)$



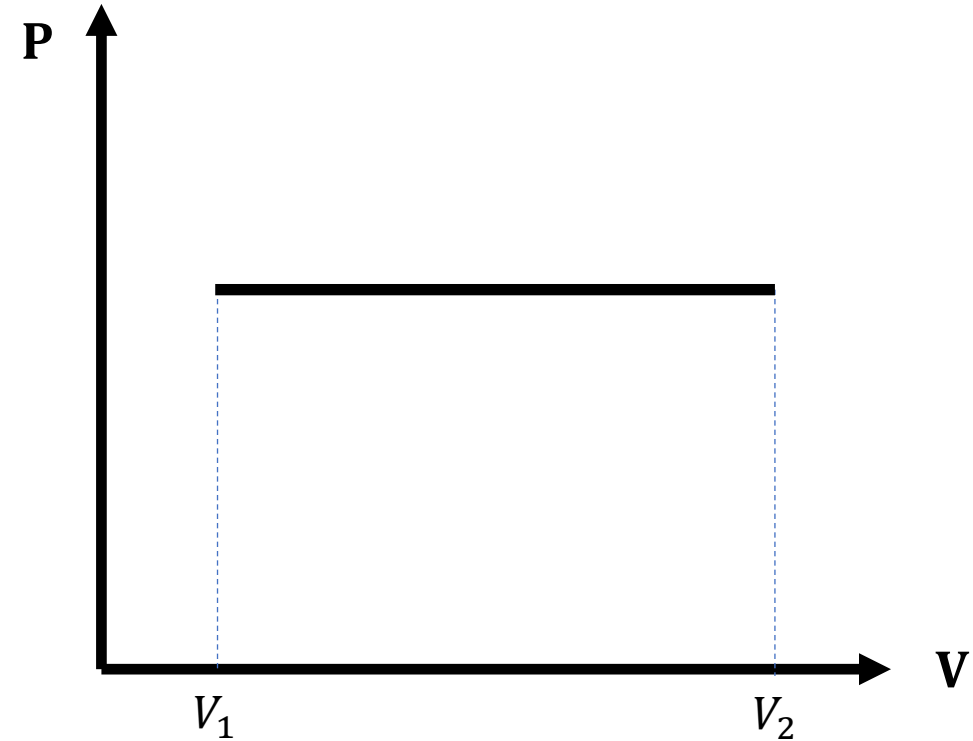
Isobaric process

$$dU = -PdV + \delta Q$$

$$C_V dT = -PdV + C_P dT$$

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

Additional heat to compensate for the work by (gas expansion)

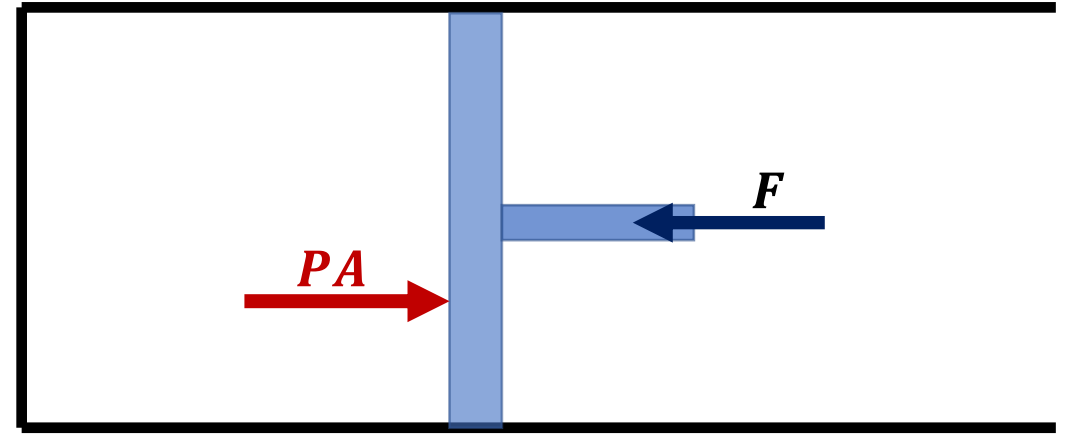


Gas equation of state: $PV = nRT$

$$C_P = C_V + nR$$

Reversible gas expansion

$$dU = -PdV + \delta Q$$



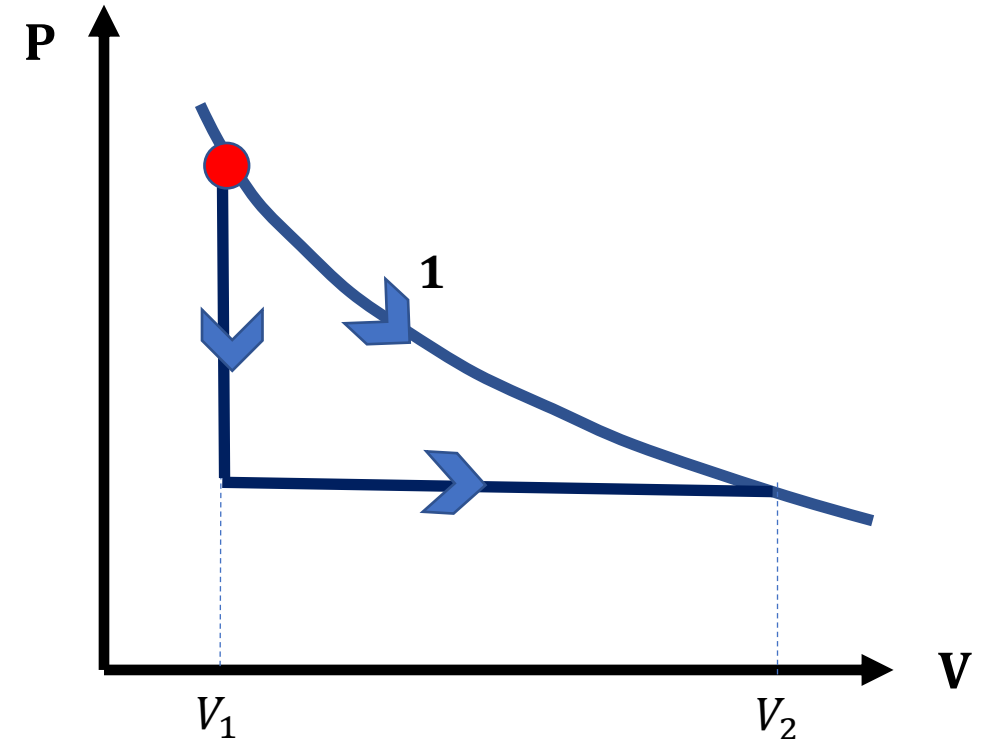
1. Isothermal path

$$T_1 = T_2 \rightarrow U_1 = U_2$$

$$\delta Q \big|_{path\ 1} = -\delta W \big|_{path\ 1}$$

$$Q = nRT \ln \frac{V_2}{V_1} > 0$$

Heat flows into the system (heat is absorbed)



Reversible gas expansion

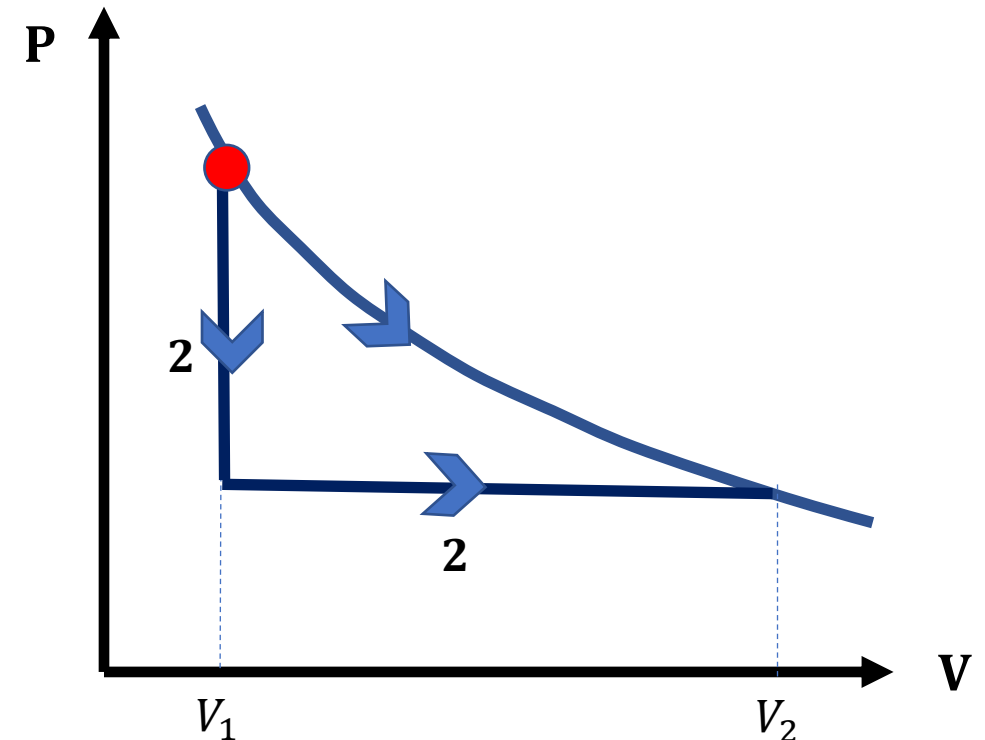
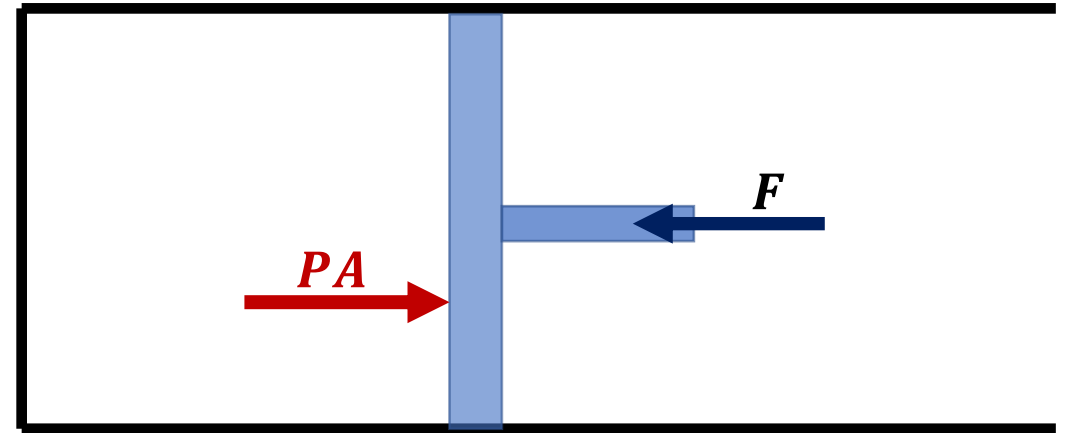
$$dU = -PdV + \delta Q$$

2. Isocoric+Isobaric path

$$\delta Q \Big|_{\text{path 2}} = PdV \Big|_{\text{path 2}}$$

$$Q = P_2(V_2 - V_1) > 0$$

Heat flows into the system (heat is absorbed)



Adiabatic Process

$$\delta Q = 0 \rightarrow dU = \delta W$$

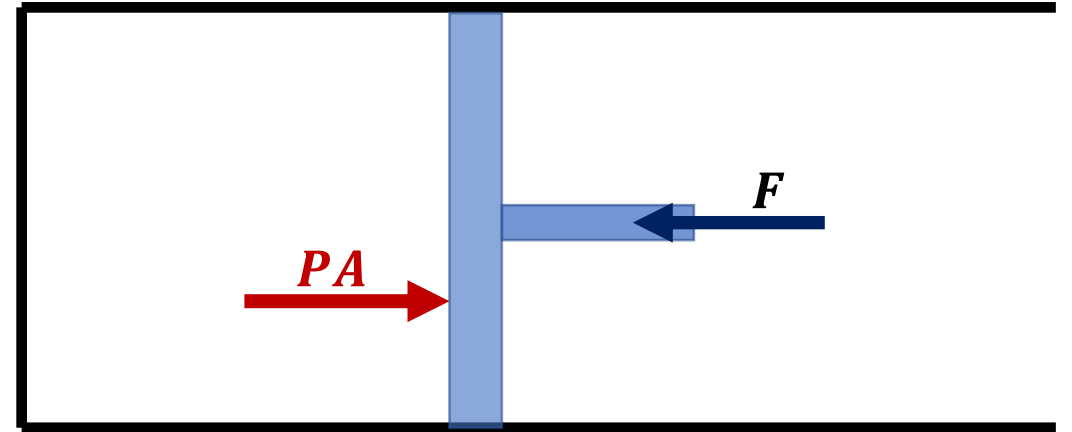
$$C_V dT = -PdV$$

$$C_V \frac{dT}{T} = -nR \frac{dV}{V}$$

$$C_V \ln T + nR \ln V = \text{const.}$$

$$TV^{\frac{C_P}{C_V}-1} = \text{const.}$$

$$PV^{\frac{C_P}{C_V}} = \text{const.}$$

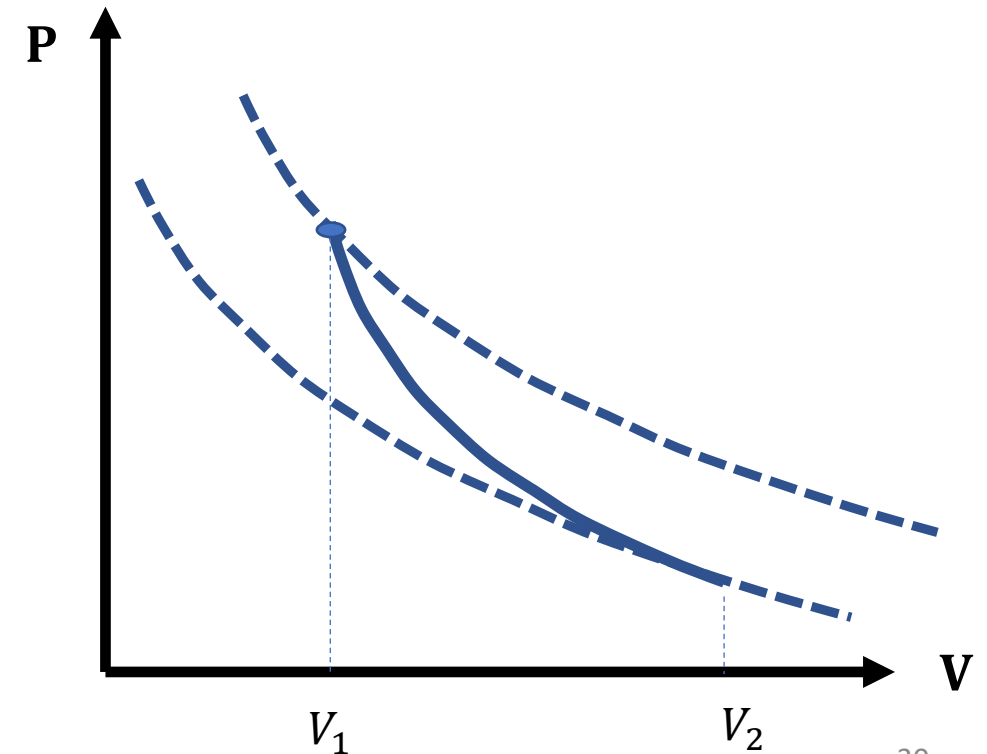
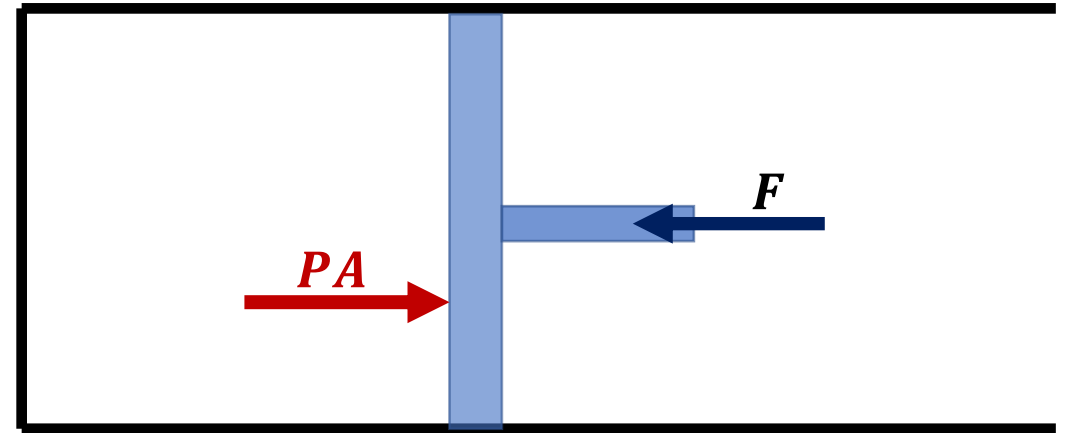


Adiabatic expansion

$$TV^{\frac{C_P}{C_V}-1} = \text{const.}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P}{C_V}-1} < 1$$

Gas cools upon an adiabatic expansion



Joule-Thomson expansion

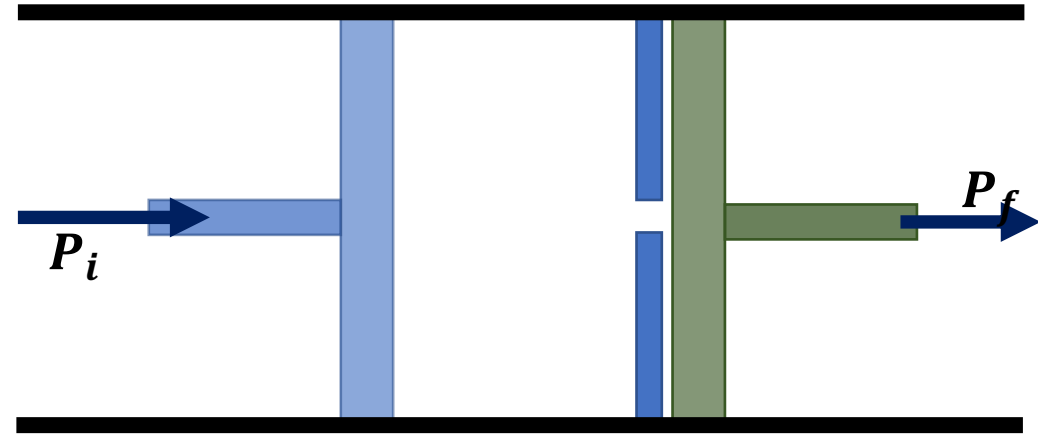
$$Q = 0 \rightarrow dU = dW$$

Work done on the gas:

$$W_i = - \int_{V_i}^0 P_i dV = P_i V_i$$

Work done by the gas:

$$W_f = - \int_0^{V_f} P_f dV = -P_f V_f$$



Joule-Thomson expansion

$$Q = 0 \rightarrow \Delta U = W$$

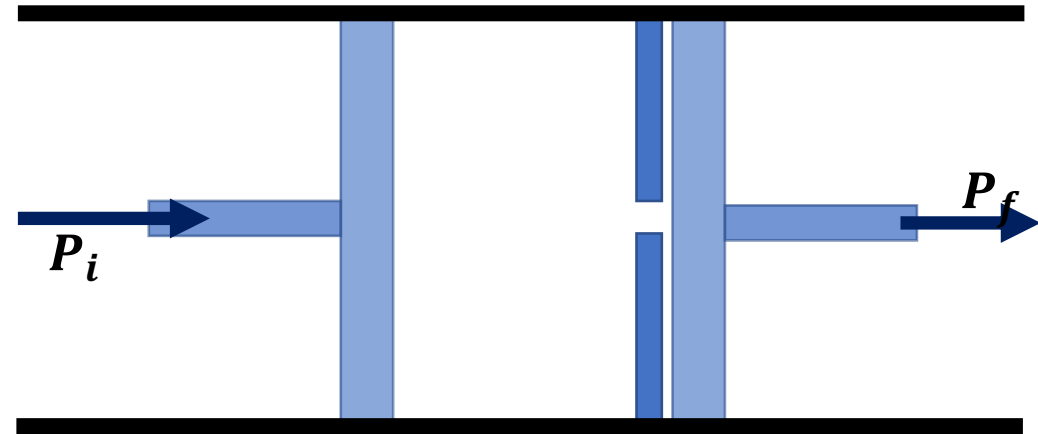
Total work

$$W = P_i V_i - P_f V_f$$

$$U_f - U_i = P_i V_i - P_f V_f$$

Constant Enthalpy

$$H = U + PV$$



«Enthalpy Capacity»

$$c_P = \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P = \frac{dH}{dT}$$

Summary

- **Temperature** is thermodynamic state variable for a system at *thermal equilibrium*
- **Heat** Q and **work** W are «energies in transit»
- **First law of thermodynamics**

The change in the internal («stored») energy equal the sum of «energies in transit »

$$\Delta U = W + Q$$

- heat capacity comes in two flavors

$$C_V = \frac{dU}{dT} \quad C_P = \frac{dH}{dT}$$