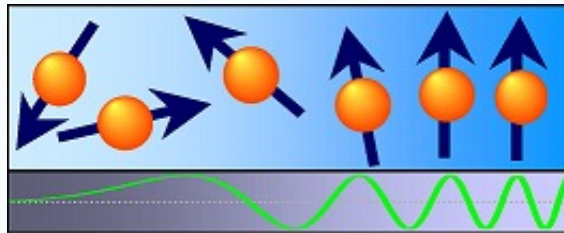


Experimental Physics EP2

Thermodynamics

– Heat –

Heat capacity, 1st law of thermodynamics



<https://bloch.physgeo.uni-leipzig.de/amr/>

Heat capacity

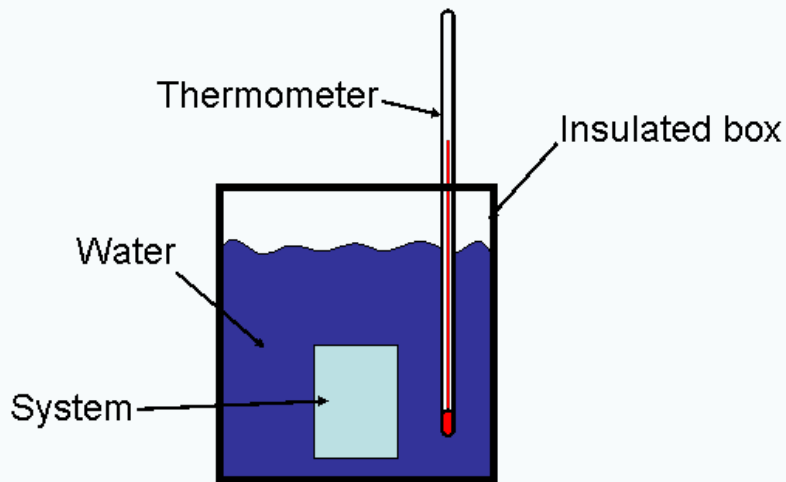


$$Q = C \cdot \Delta T = mc\Delta T$$

C – heat capacity;
 c – specific heat

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

1 kilocalorie (kcal) – the amount of heat required to increase temperature of 1 kg of water by 1°C.



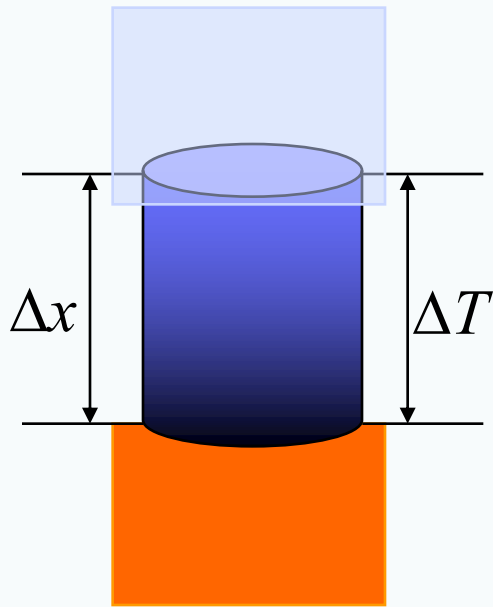
$$Q_{out} = m_s c_s (T_{si} - T_{sf})$$

||

$$Q_{in} = \sum m_i c_i (T_{if} - T_{ii})$$

Substance	Phase	c_p $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$	c_v $\text{J}\cdot\text{cm}^{-3}\cdot\text{K}^{-1}$
Hydrogen	gas	14.30	
Ammonia	liquid	4.700	3.263
Water at 25 °C	liquid	4.1813	4.1796
Water at 100 °C	liquid	4.1813	4.2160
Water vapor 100 °C	gas	1.93	
Methanol	liquid	2.597	—
Paraffin wax	solid	2.5	2.325
Gasoline	liquid	2.22	1.64
Wood	solid	1.2-2.3	
Helium	gas	5.19	
Aluminum	solid	0.897	2.422
Glass	solid	0.84	
Copper	solid	0.385	3.45
Gold	solid	0.129	2.492
Lead	solid	0.129	1.44

Transfer of thermal energy - conductivity



$\frac{dT}{dx}$ - temperature gradient

$\frac{dQ}{dt}$ - thermal current

$$I \equiv \frac{dQ}{dt} = kA \frac{dT}{dx}$$

k - thermal conductivity

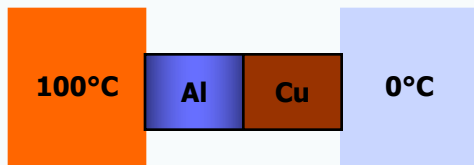
$[I] = \text{Watt, J/s}$ $[k] = \text{W/(m} \cdot \text{K)}$

$$\Delta T = \frac{\Delta x}{kA} I \equiv RI$$

R - thermal resistance

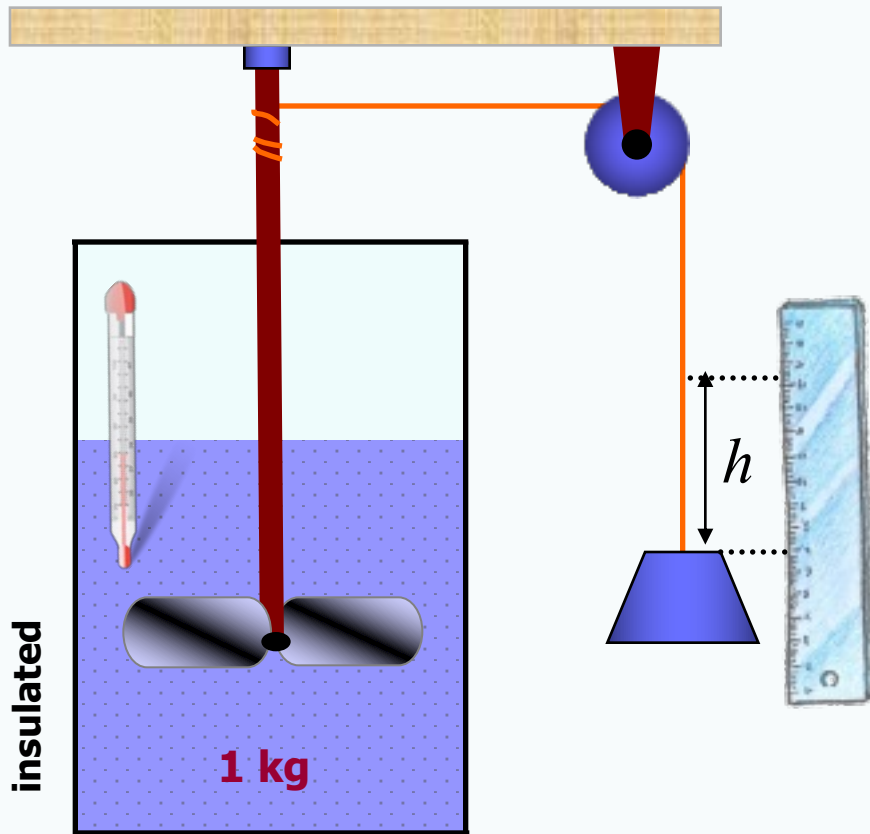
$$R_{seq} = \sum R_i$$

$$R_{par}^{-1} = \sum R_i^{-1}$$



Material	Thermal Conductivity W/m-K
Air at 0 C	0.024
Aluminum	205.0
Brass	109.0
Concrete	0.8
Copper	385.0
Glass, ordinary	0.8
Gold	310
Ice	1.6
Lead	34.7
Water	0.56
Polystyrene expanded	0.03
Silver	406.0
Styrofoam	0.01
Steel	50.2
Wood	0.12-0.04

The first law of thermodynamics



$$|Q| = mc\Delta T$$

$$4.18 \times 10^3 = 9.8 \cdot h$$

$$|W| = mgh$$

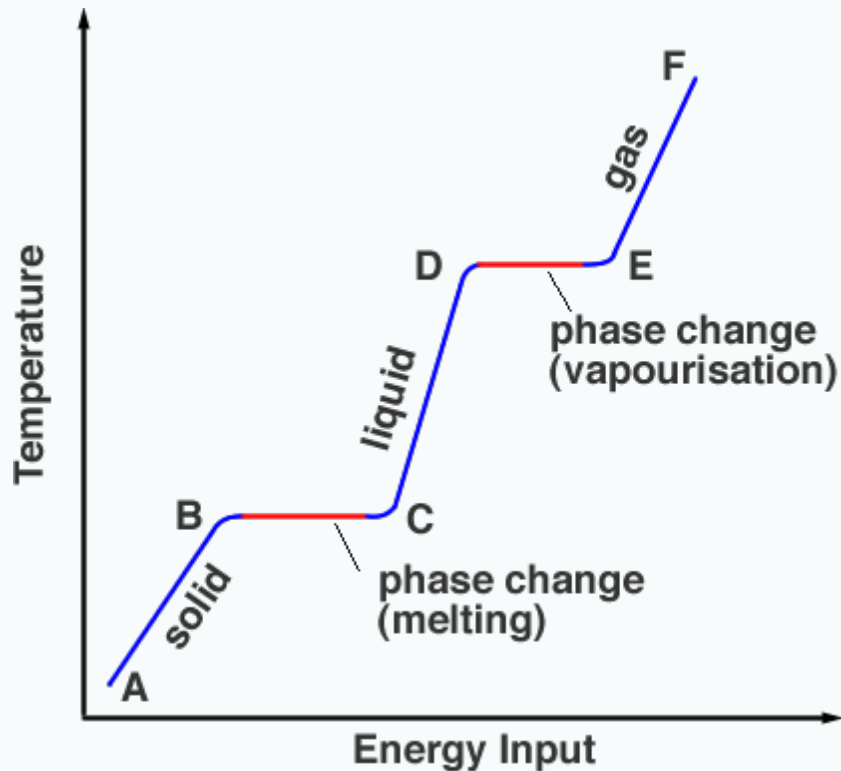
$$h = 426 \text{ m} \quad \text{- to increase temperature of 1 kg water by } 1^\circ\text{C}$$

Latent heat

$$Q = mL$$

L_v – latent heat of vaporization

L_m – latent heat of melting



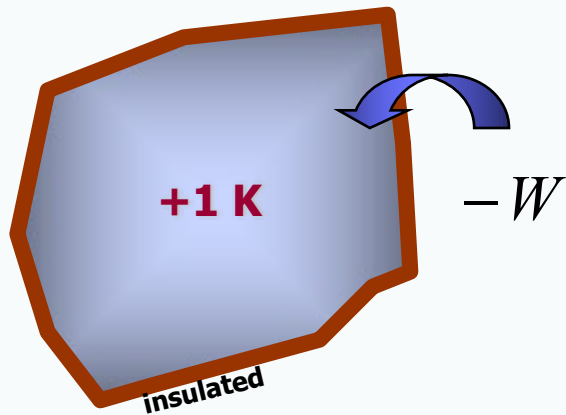
Substance	Specific latent heat of fusion kJ/kg	°C	Specific latent heat of vaporization kJ/kg	°C
Water	334	0	2258	100
Ethanol	109	-114	838	78
Chloroform	74	-64	254	62
Mercury	11	-39	294	357
Copper	205	1629	4726	3112
Hydrogen	60	-259	449	-253
Oxygen	14	-219	213	-183
Nitrogen	25	-210	199	-196

Sublimation



The first law of thermodynamics

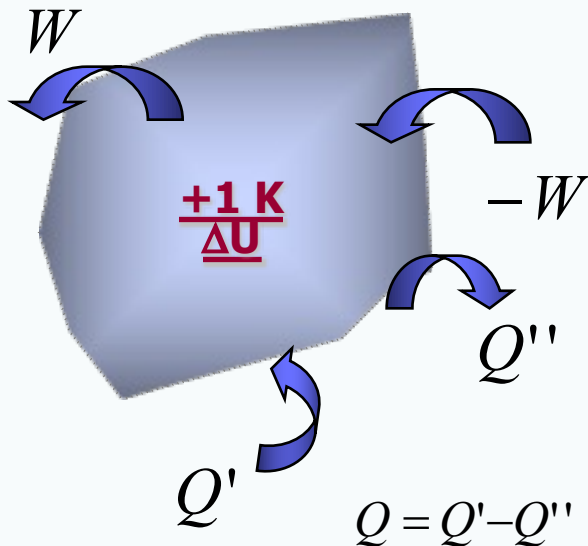
$$Q = \Delta U + W$$



The **net heat** added to system equals the **change of the internal energy** of the system plus the **work done by the system**.

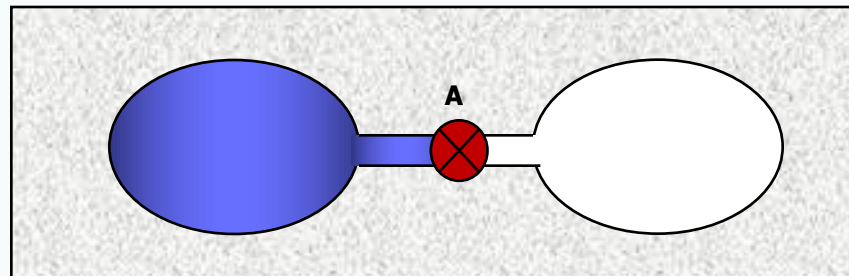
U is the function of the system state, while W and Q are not!

$$\delta Q = dU + \delta A$$

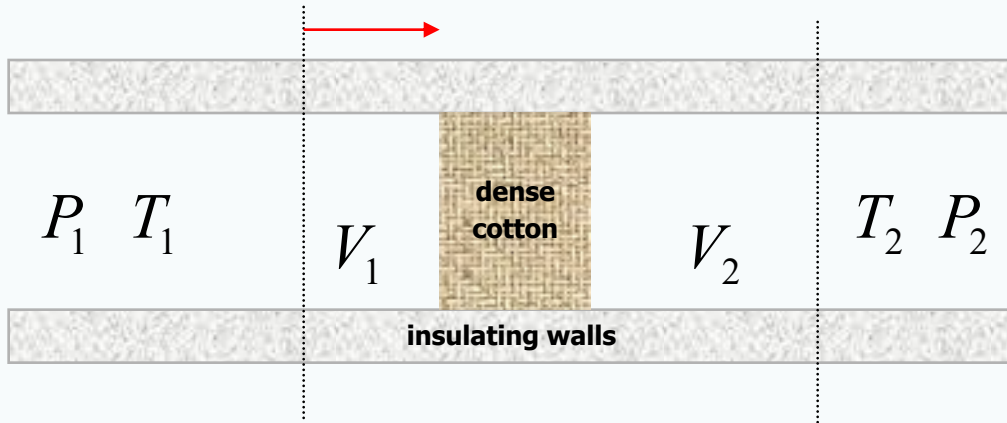


$$E_K = \frac{3}{2} NkT = \frac{3}{2} \nu RT = U$$

Kinetic energy of ν moles of ideal gas.



Joule-Thomson effect



- Stationary flow of a gas through a plug is called Joule-Thomson process.
- Change of temperature during this process – Joule-Thomson effect.

- The pressures on both sides are kept constant.
- Due to cotton, the flow is slowed down so that the molecular kinetic energy is negligible.
- That means that on both sides the gas is in thermodynamic equilibrium.
- Given a time for equilibration, a stationary flow is established.
- In the stationary state, temperatures on both sides also become constant.

Net work done by the gas: $W = -P_1 A \Delta x_1 + P_2 A \Delta x_2 = P_2 V_2 - P_1 V_1$

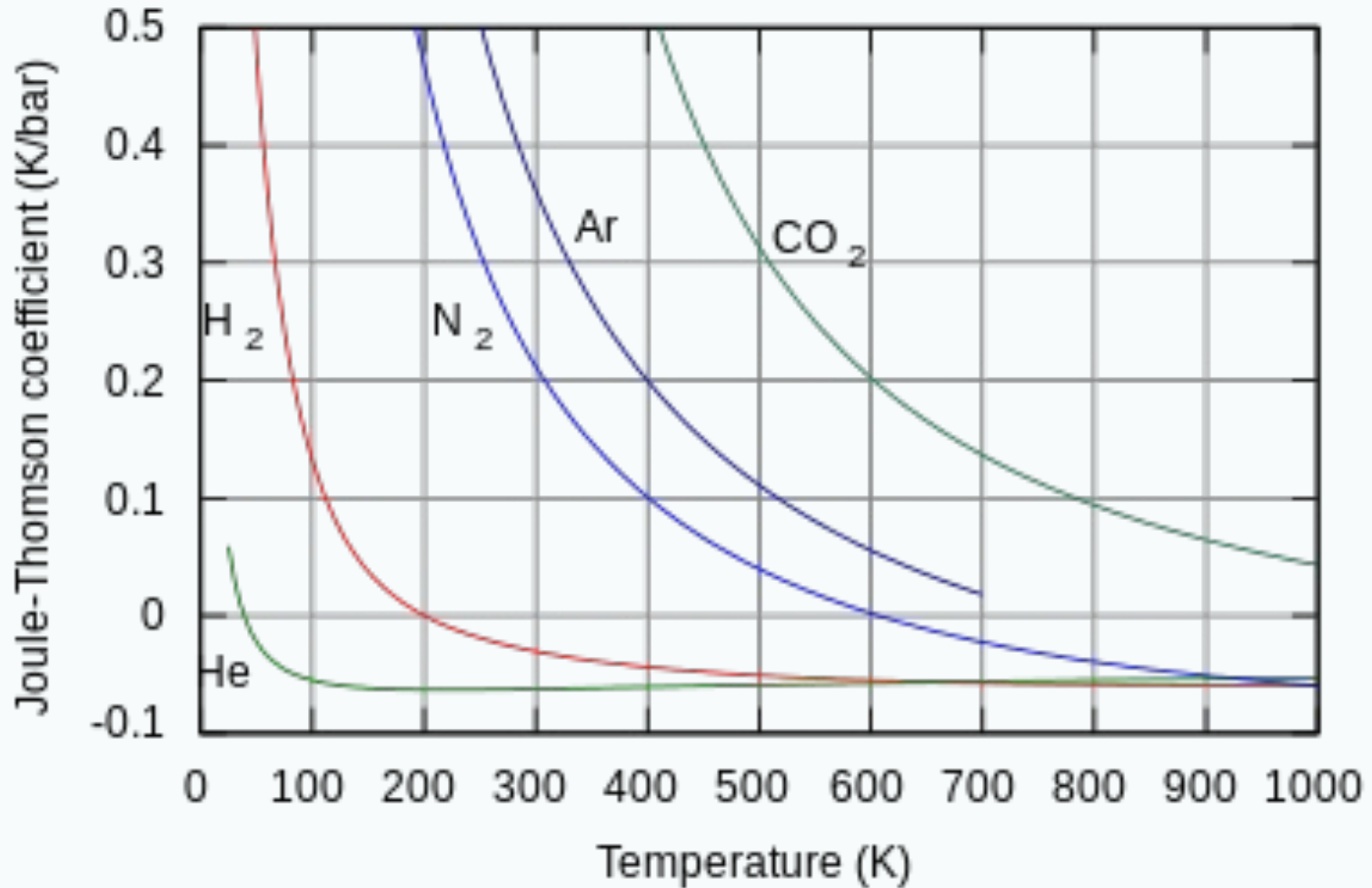
$$Q = \Delta U + W \Rightarrow U_2 - U_1 + P_2 V_2 - P_1 V_1 = 0$$

$$U_2 + P_2 V_2 = U_1 + P_1 V_1 = \text{const}$$

$$I \equiv U + PV \text{ - enthalpy}$$

If $T_2 = T_1$, as observed in experiments for near-ideal gases: $U(T, V_1) = U(T, V_2)$

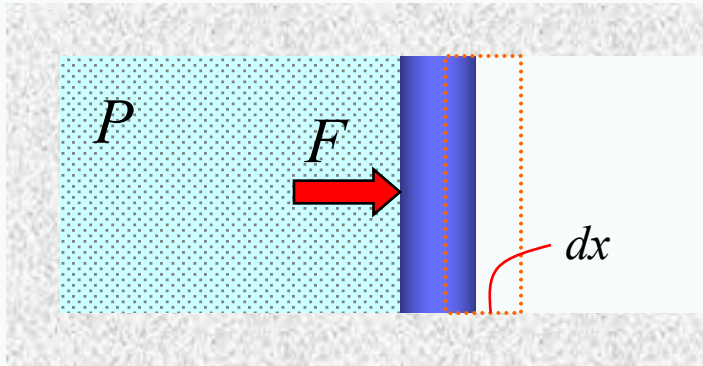
Joule-Thomson effect



$$U_2 + P_2V_2 = U_1 + P_1V_1 = \text{const}$$

$$\mu_T = \left(\frac{\partial T}{\partial P}\right)_I$$

Heat capacities



$$C_p = C_v + R$$

Mayer's equation

TABLE 21.2 Molar Specific Heats of Various Gases

Molar Specific Heat (J/mol · K)^a

Gas	C_p	C_v	$C_p - C_v$	$\gamma = C_p/C_v$
Monatomic Gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic Gases				
H ₂	28.8	20.4	8.33	1.41
N ₂	29.1	20.8	8.33	1.40
O ₂	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl ₂	34.7	25.7	8.96	1.35
Polyatomic Gases				
CO ₂	37.0	28.5	8.50	1.30
SO ₂	40.4	31.4	9.00	1.29
H ₂ O	35.4	27.0	8.37	1.30
CH ₄	35.5	27.1	8.41	1.31

1. Constant volume heating: $\delta_v Q = C_v dT$

$$dU = C_v dT \quad \text{no work is done (dV=0)}$$

2. Constant pressure heating: $\delta_p Q = C_p dT$

$$C_p dT = dU + PdV = dU + RdT$$

dU is the same for both processes!

$$C_p dT = C_v dT + RdT$$

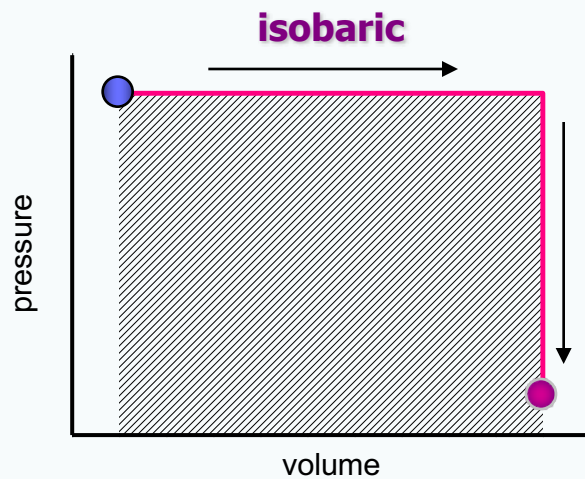
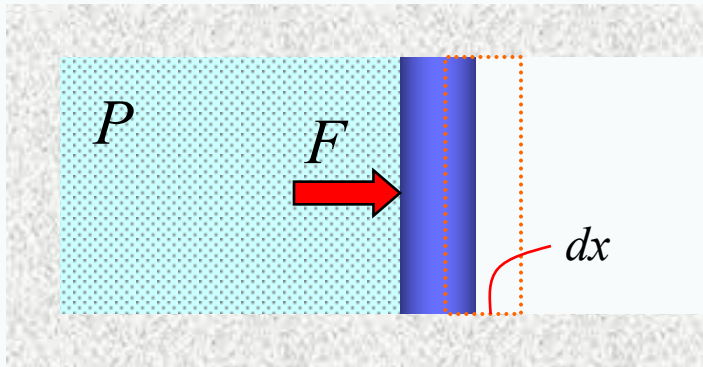
$$Q = \Delta U + W$$

PV-diagram for gas

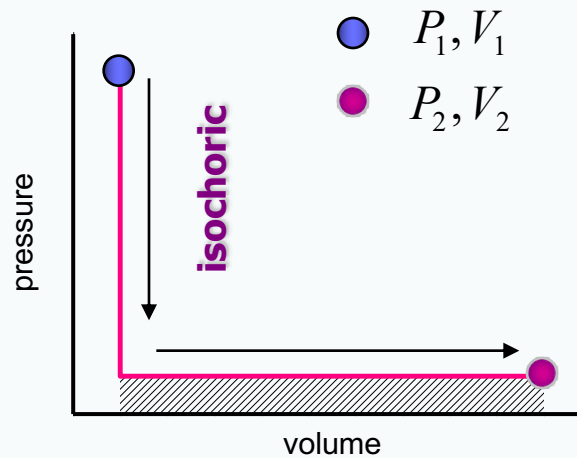
Very slow, *quasistatic* process of the volume change.

$$\delta W = F dx = P A dx = P dV$$

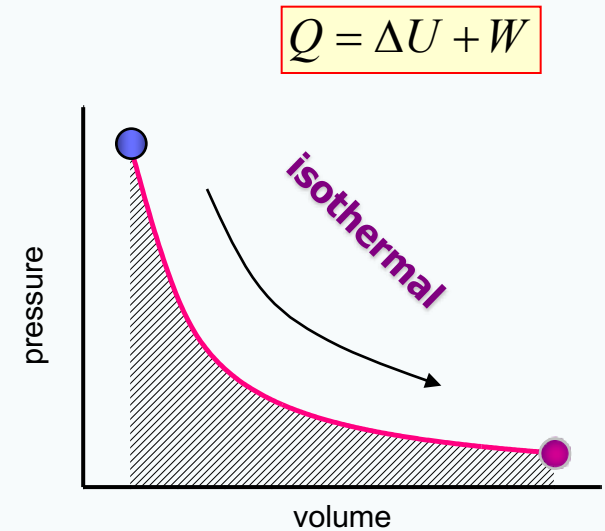
$$W = \int P dV \quad \text{- the work done by gas}$$



$$W = P_1(V_2 - V_1)$$



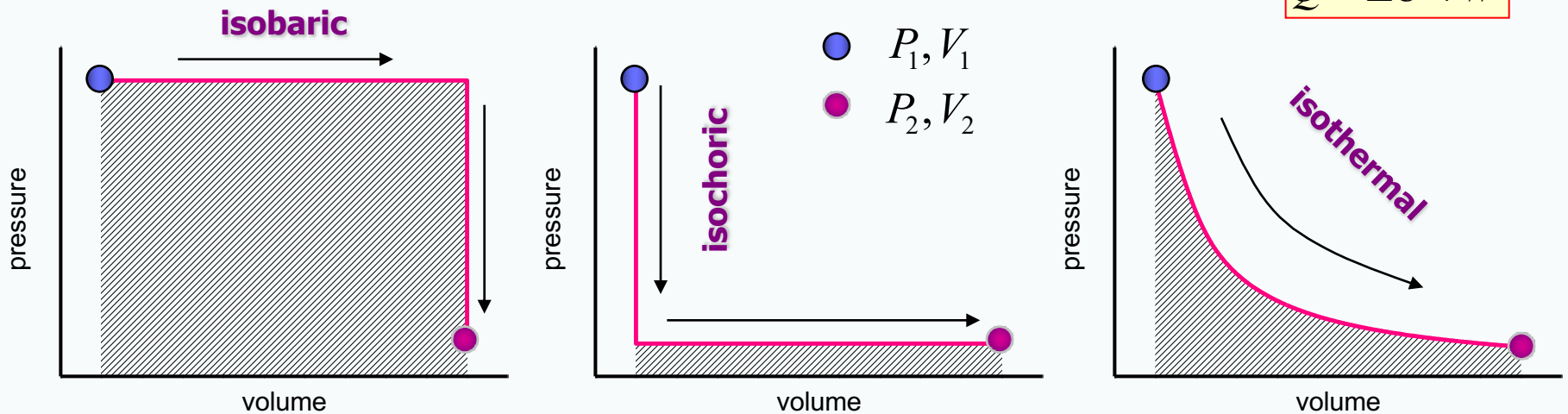
$$W = P_2(V_2 - V_1)$$



$$W = \nu RT \ln \frac{V_2}{V_1}$$

$$Q = \Delta U + W$$

Adiabatic processes

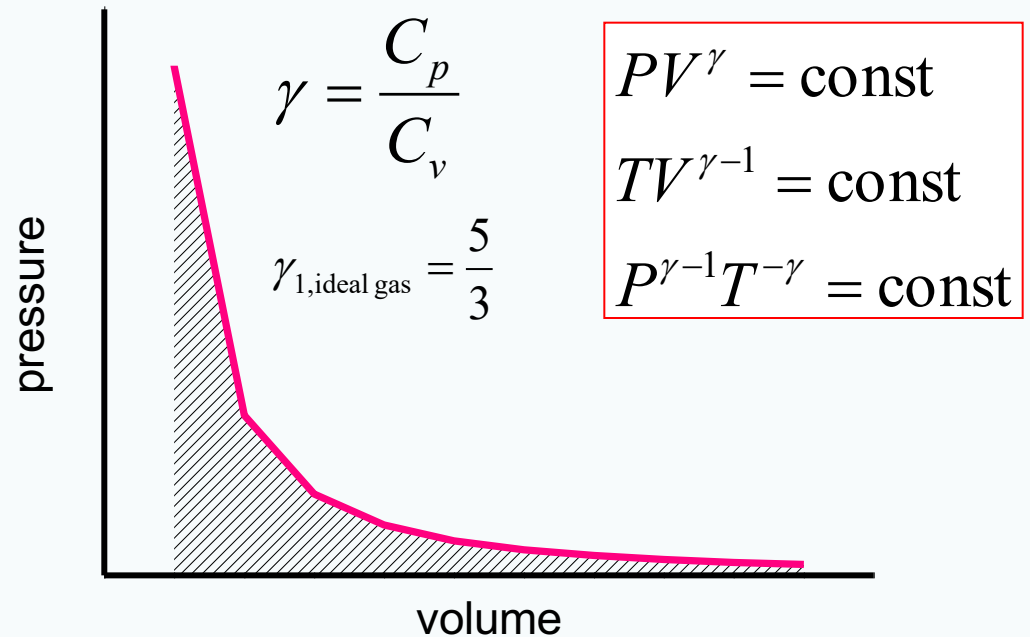


Process occurring without supply or removal of heat is called **adiabatic** process.

$$C_v dT + PdV = 0$$

$$dT = d\left(\frac{PV}{\nu R}\right) = \frac{PdV + VdP}{C_p - C_v}$$

$$C_p PdV + C_v VdP = 0$$



Some mathematics

$$Q = \Delta U + W$$

$$C = \frac{\delta Q}{dT}$$

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

$$U = U(T, V)$$

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

$$C = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] \cdot \frac{dV}{dT}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

Ideal gas:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\nu R}{P}$$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_p = \left(\frac{\partial I}{\partial T}\right)_P$$

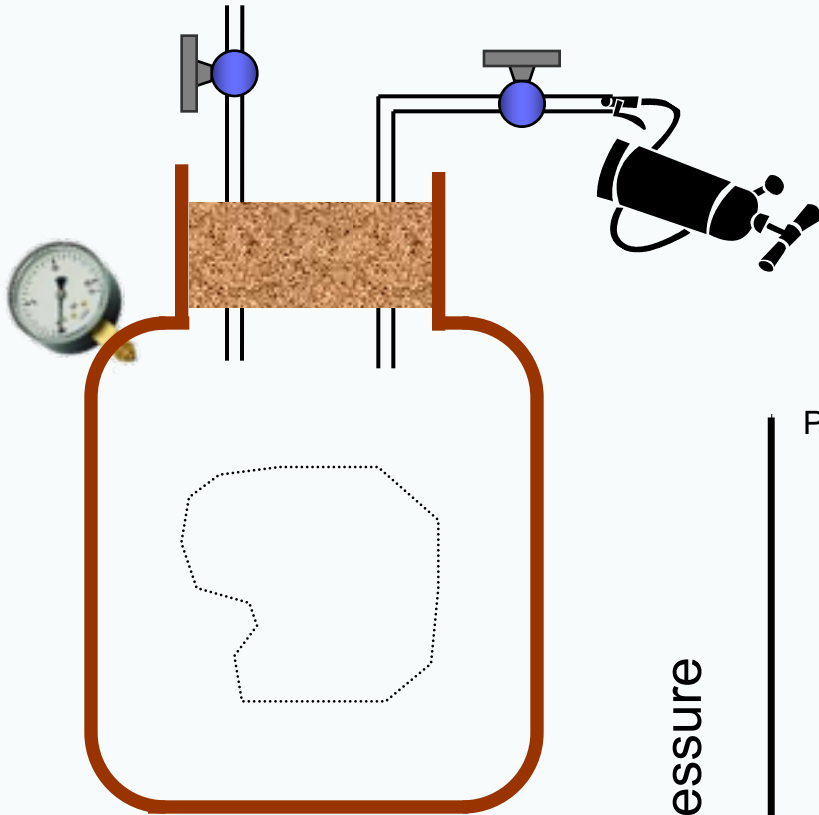
$$C_p - C_v = \nu R$$

Mayer's equation

$$I \equiv U + PV \quad \text{- enthalpy}$$

Assessing the adiabatic exponent

Clement-Desormes experiment



$$\gamma P(V_2 - V_1) + V(P_0 - P_1) = 0$$

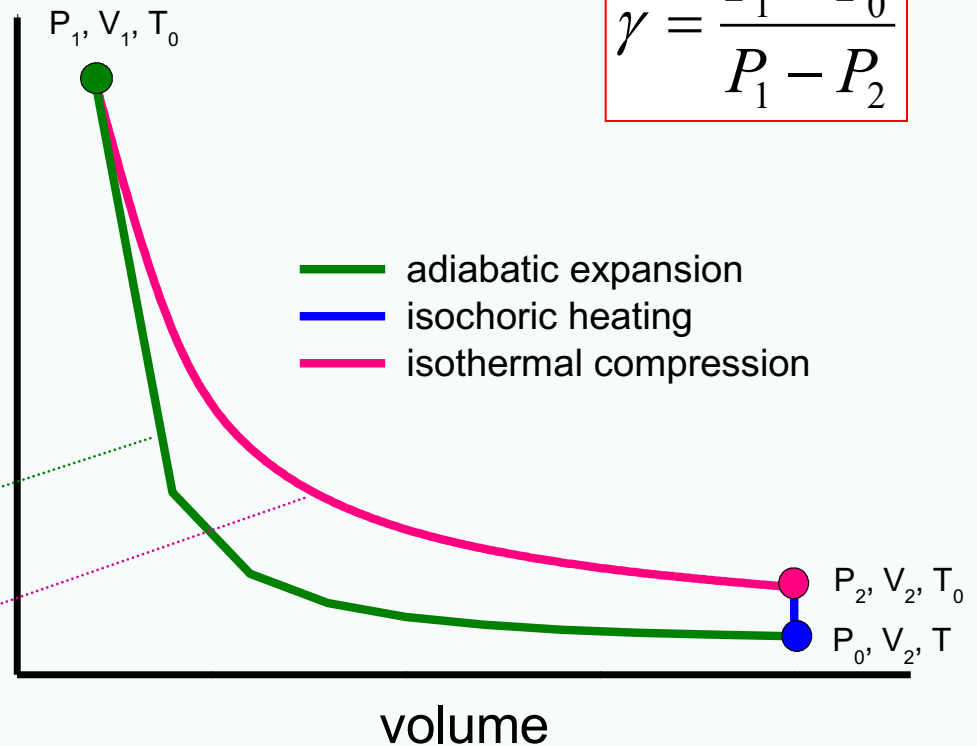
$$P(V_2 - V_1) + V(P_2 - P_1) = 0$$

$$\gamma = \frac{P_1 - P_0}{P_1 - P_2}$$

$$\gamma PdV + VdP = 0$$

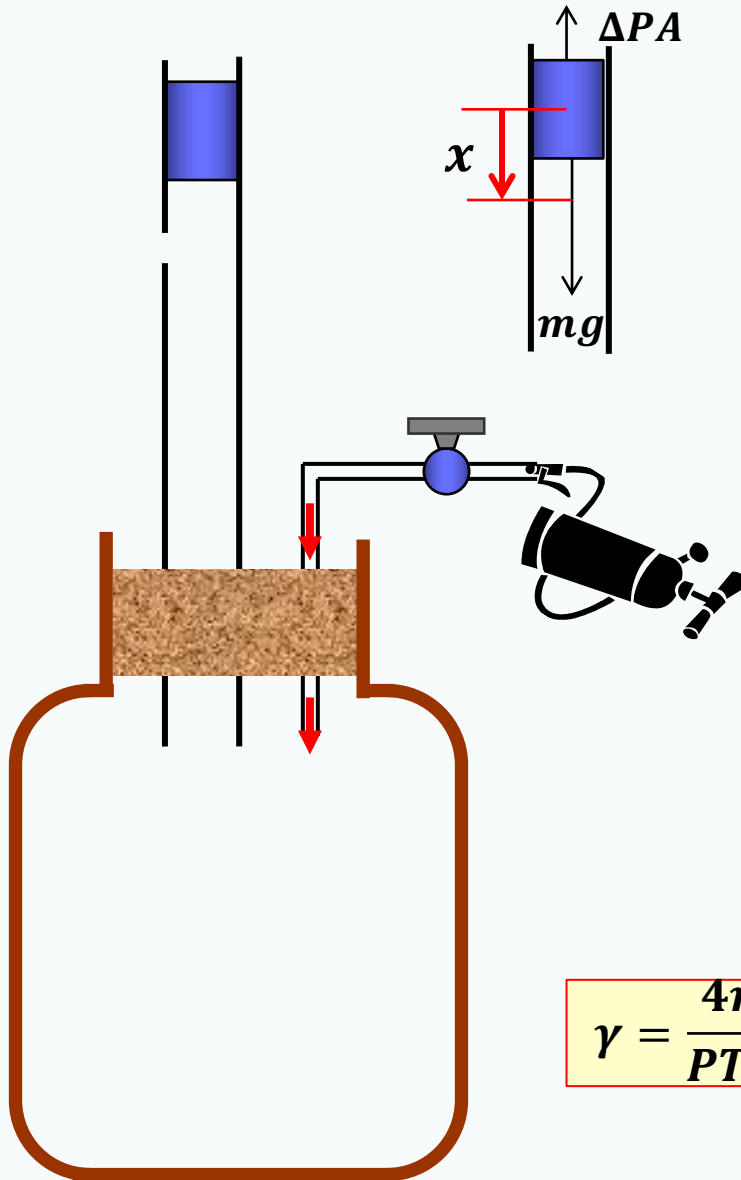
$$PdV + VdP = 0$$

pressure



Assessing the adiabatic exponent

Flammersfeld oscillator



$$m \frac{d^2 x}{dt^2} = mg - \Delta P A$$

$$\Delta P = P_r + \frac{mg}{A} - P_0 = \Delta P_r + \frac{mg}{A}$$

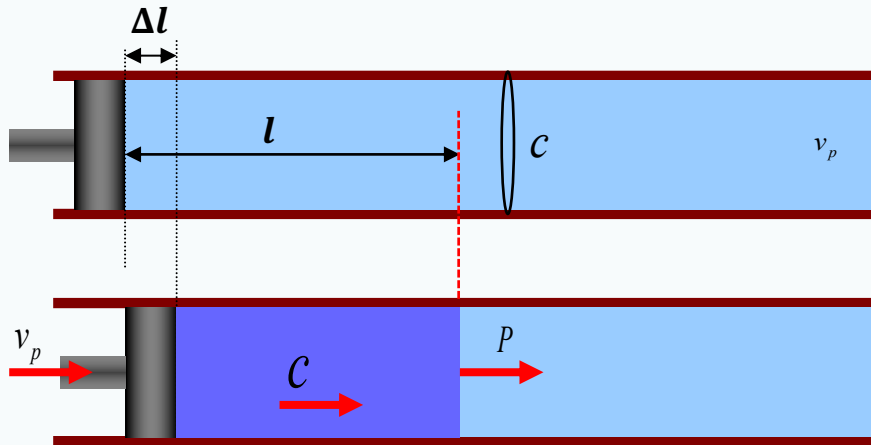
$$P_r V^\gamma = \text{const} \quad \text{- adiabatic process}$$

$$\Delta P_r = -P_r \gamma \frac{\Delta V}{V} = P_r \gamma \frac{Ax}{V}$$

$$m \frac{d^2 x}{dt^2} = -\frac{P_r \gamma A^2}{V} x \quad \omega^2 = \frac{P_r \gamma A^2}{mV}$$

$$\gamma = \frac{4mV}{PT^2 r^4} = \frac{4 \cdot 4.6 \times 10^{-3} \cdot 1.13 \times 10^{-3}}{10^5 \cdot (5.95 \times 10^{-3})^4 \cdot T^2} = \frac{0.166}{T^2}$$

Assessing the adiabatic exponent



$$F = (P - P_0)A = \frac{d(mv_p)}{dt} = \frac{d}{dt}(Act\rho \cdot v_p)$$

$$\Delta P = c\rho v_p \quad \Delta P = -A \frac{\Delta V}{V} = -A \frac{v_p}{c}$$

$$c^2 = \frac{K}{\rho} \quad \Delta P = \frac{dP}{dV} \Delta V \quad A = -V \frac{dP}{dV} \equiv K$$

$$c^2 = \frac{dP}{d\rho} \quad A = \rho \frac{dP}{d\rho} \quad K = -V \left(\frac{\partial P}{\partial V} \right)_T$$

Bulk modulus

Speed of sound

According to Newton:

$$c_N = \sqrt{\frac{dP}{d\rho}} = \sqrt{\left(\frac{\partial P}{\partial \rho} \right)_T} = \sqrt{\frac{RT}{M}}$$

According to Laplace:

$$c_L = \sqrt{\left(\frac{\partial P}{\partial \rho} \right)_{adiabatic}}$$

$$\left(\frac{\partial P}{\partial \rho} \right)_{adiabatic} = \gamma \frac{P}{\rho} = \gamma \left(\frac{\partial P}{\partial \rho} \right)_T$$

$$\gamma = \left(\frac{c_L}{c_N} \right)^2 = \frac{Mc^2}{RT}$$

$$\gamma_{air} = \frac{28.97 \times 10^{-3}}{8.31 \cdot 295} c^2 \approx 1.187 \times 10^{-5} \cdot 343^2 = 1.39$$

To remember!

- **The first law of thermodynamics simply states the conservation of total energy.**
- **Heat added to a system is equal to work done by the system plus change of its internal energy.**
- **The internal energy of ideal gas is its kinetic energy.**
- **The internal energy is a state function.**
- **Work done and heat added or extracted depend on how the system has been changed. Change of the internal energy does not!**
- **For adiabatic processes, however, the work done is also pathway-independent.**

