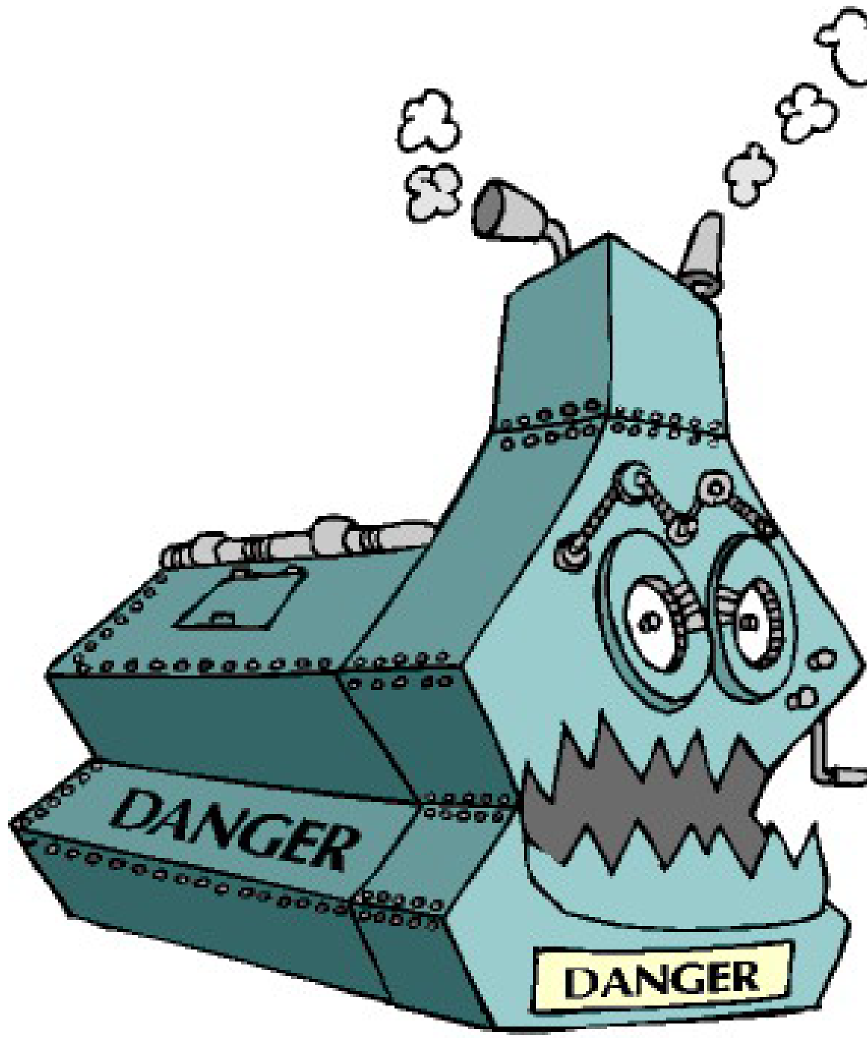
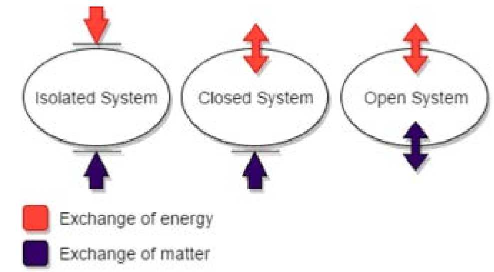
Thermodynamics



state of a system, state quantities $p, V, T, \cancel{N, n}$

systems — isolated vs. non-isolated; closed vs. open



steady state – time of relaxation

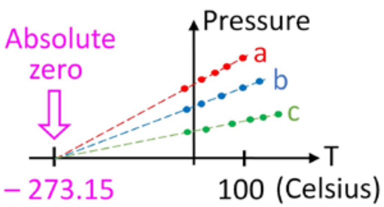
equilibrium process — reversible process — cyclic process

Temperature

based on the thermodynamic equilibrium of systems principle

Zeroth law of thermodynamics

$$T = T\left(p,V\right) \qquad p = const. \Rightarrow T = T(V) \qquad V = const. \Rightarrow T = T(p)$$



$$p = p_0\left(1+\gamma t\right)$$ gas-thermometer scale

$$\gamma = \frac{1}{273{,}15}\ ^\circ\mathrm{C}^{-1}$$ Celsius scale

absolute temperature scale $\frac{1}{\gamma} = T_0$ $T = T_0 + t$

thermodynamic scale

triple point + energy from the Carnot cycle effectivity

Perfect (ideal) gas

$$\frac{pV}{T} = \frac{p_0 V_0}{T_0} = \frac{n p_0 V_{m0}}{T_0} = \frac{n \cdot 1{,}013.10^5 \cdot 0{,}0224}{273} = n \cdot 8.314 = n \cdot R_m = const.$$

Equation of state for perfect gas

$$pV = nR_m T = N \frac{R_m}{N_A} T = NkT$$

$R_m = 8{,}314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ gas constant (molar)

$k = 1{,}380\ 66 \cdot 10^{-23}\ \mathrm{J \cdot K^{-1}}$ Boltzmann constant

Kinetic theory of gases — gas pressure

monoatomic molecule + wall perpendicular to *x* direction

$2mv_x$ change of the linear momentum due to collision

$\frac{N_i}{2V} S v_{xi} \Delta t$ molecules with **positive** velocity v_{xi} interacting with the wall during a time of Δt

$$\frac{N_i}{2V} S v_{xi} \Delta t \left(2mv_{xi}\right) = \frac{N_i}{V} S m v_{xi}^2 \Delta t = \bar{F} \Delta t \qquad p = \frac{\bar{F}}{S}$$

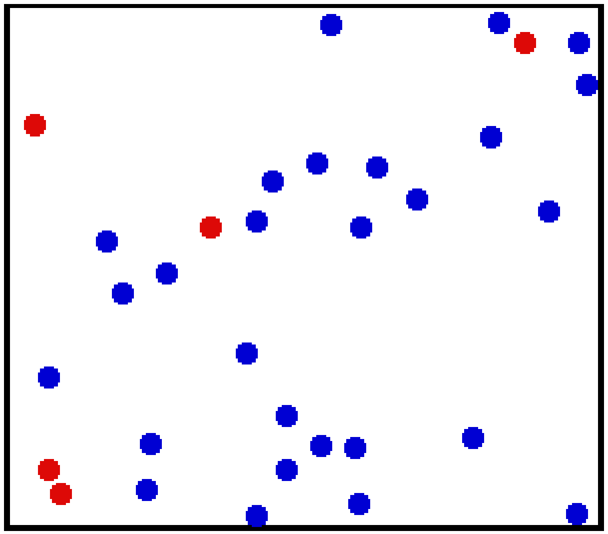
$$p_i = \frac{N_i}{V} m v_{xi}^2$$

$$p = \sum_i p_i = \sum_i \frac{N_i}{V} m v_{xi}^2 = \frac{m}{V} \sum_i N_i v_{xi}^2 \qquad N = \sum_i N_i$$

$$\overline{v_x^2} = \frac{1}{N} \sum_i N_i v_{xi}^2 \qquad \sqrt{\overline{v_x^2}}$$ *x*-component of the RMS speed

$$\overline{v^2} = \frac{1}{N}\sum_i N_i v_i^2$$

RMS speed



$$p = \frac{m}{V}\sum_i N_i v_{xi}^2 = \frac{N}{V} m\overline{v_x^2} = \frac{1}{3}\frac{N}{V} m\overline{v^2}$$

$$pV = Nm\overline{v_x^2} = 2N\left(\frac{1}{2}m\overline{v_x^2}\right) = NkT$$

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}kT$$

Equipartition theorem

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

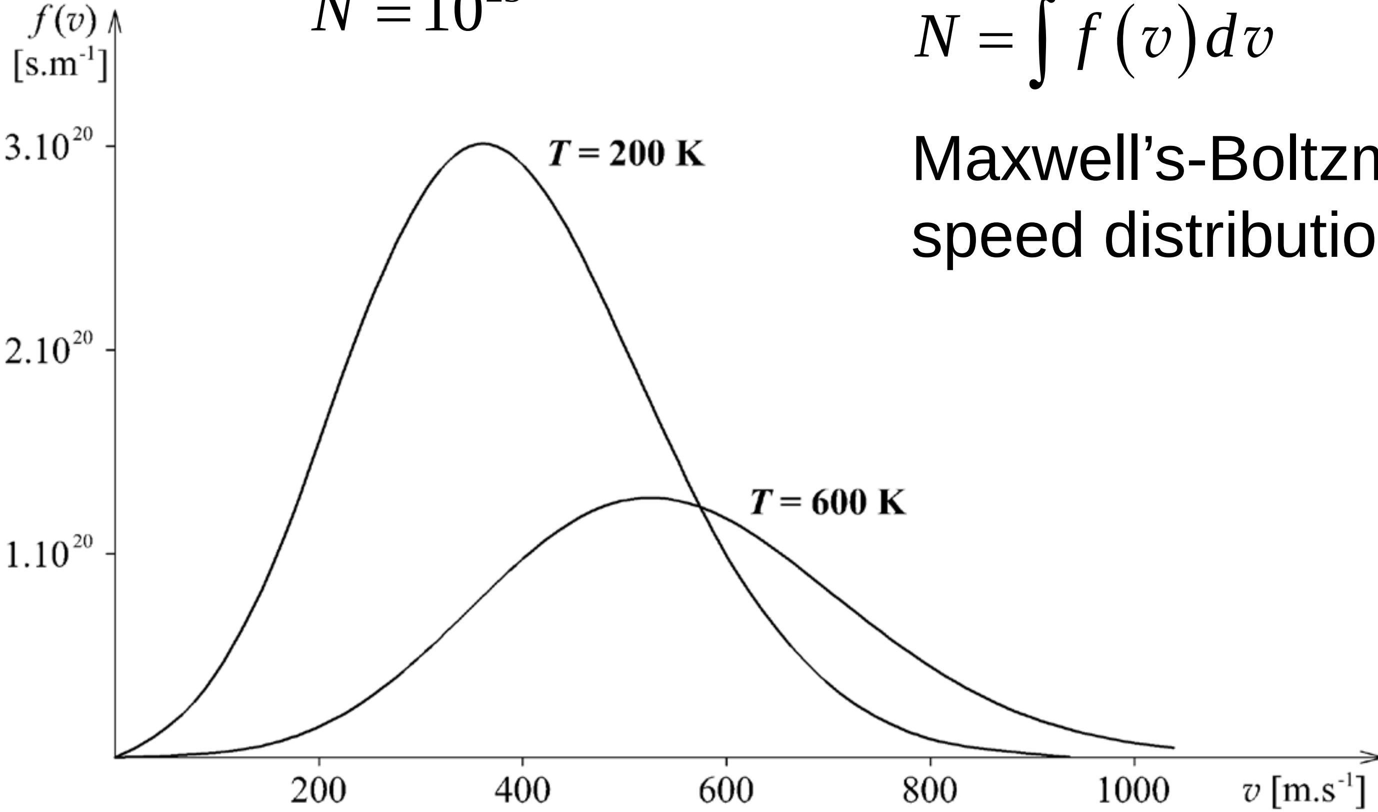
monoatomic gas molecule

diatomic molecule $W_k = \frac{5}{2}kT$

Internal energy of perfect gas $U = Ns\frac{1}{2}kT = \frac{s}{2}nR_m T$

Speed distribution of molecules

$$N = 10^{23}$$



$$N = \int f(v)\,dv$$

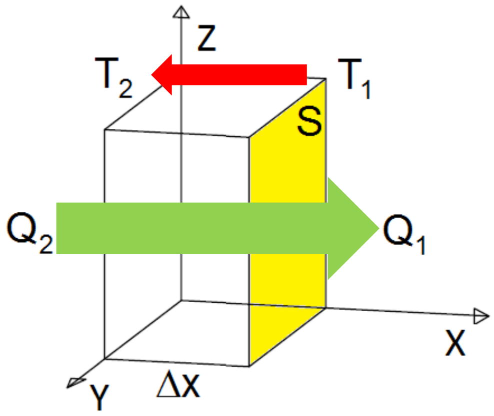
Maxwell's-Boltzmann speed distribution

Van der Waals Equation

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = R_m T$$

Differential heat equation - Conduction

heat transfer ΔQ decreased by Δx layer heat-up



$$Q_1 - Q_2 = (q_1 - q_2)S\Delta\tau = -\Delta q S \Delta\tau$$

$q \approx$ areal heat flux density

$$Q_1 - Q_2 = c\Delta m \Delta T = c\rho\Delta V \Delta T = c\rho S \Delta x \Delta T = -\Delta q S \Delta\tau$$

$$c\rho \frac{\Delta T}{\Delta\tau} = -\frac{\Delta q}{\Delta x}$$

$$q = -\lambda \,\mathrm{grad}\, T = -\lambda \nabla T$$

Fourier's law

$$c\rho \frac{\partial T}{\partial\tau} - \lambda\nabla^2 T = P_V$$

c specific heat capacity [J·kg^{-1}·K^{-1}]

ρ density of matter [kg·m^{-3}]

λ thermal conductivity [W·m^{-1}·K^{-1}]

P_V volumetric heat power density [W·m^{-3}]

Stationary conduction

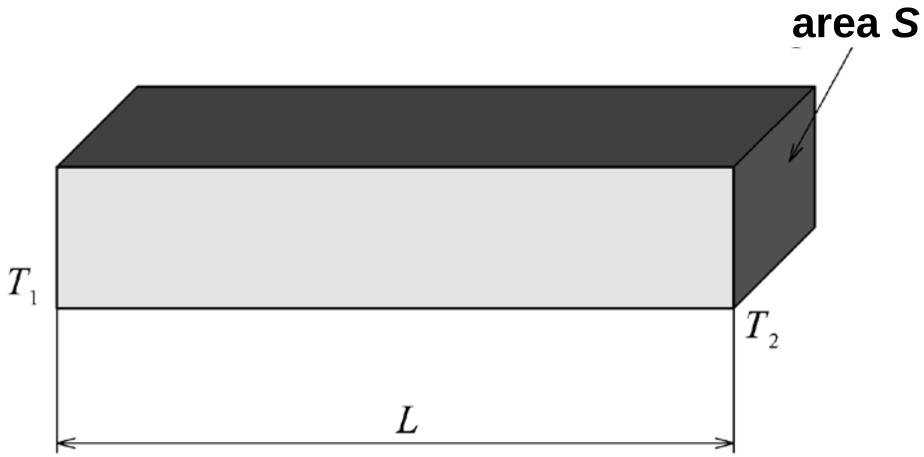
1. time independent, no heat source
2. one-dimensional heat transfer

$$\nabla^2 T = 0 \quad \Rightarrow \quad \frac{dT}{dx} = const.$$

$$T(x) = \frac{T_2 - T_1}{L} x + T_1$$

$$\frac{dQ}{dt} = -\lambda S \frac{dT}{dx}$$

$$Q_\tau = \lambda \frac{T_2 - T_1}{L} S$$



$$R_T = \frac{L}{\lambda S}$$ thermal resistance

Convection and Radiation

Convection heat transferred by a fluid

Radiation

$$\frac{d^2W}{dS\,dt} = \varepsilon\sigma T^4$$

$$\sigma = 5{,}67 \cdot 10^{-8}\,\mathrm{W} \cdot \mathrm{m}^{-2} \cdot \mathrm{K}^{-4}$$

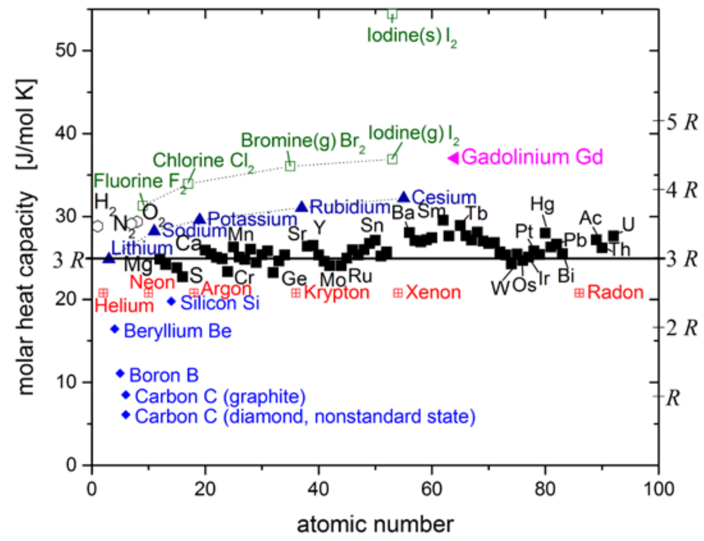
ε surface emissivity

$$P = \varepsilon\sigma S T^4$$ Stefan-Boltzmann law of radiation

heat capacity of matter $$C = \frac{dQ}{dT}$$

specific heat capacity $$c = \frac{C}{m}$$

molar heat capacity $$C_m = \frac{C}{n}$$



substance	aluminium	copper	gold	silver	zinc	mercury	ethyl alcohol
c [$\mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$]	0,900	0,386	0,126	0,233	0,387	0,140	2,4
C_m [$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$]	24,3	24,5	25,6	24,9	25,2	28,3	111

Dulong-Petit law

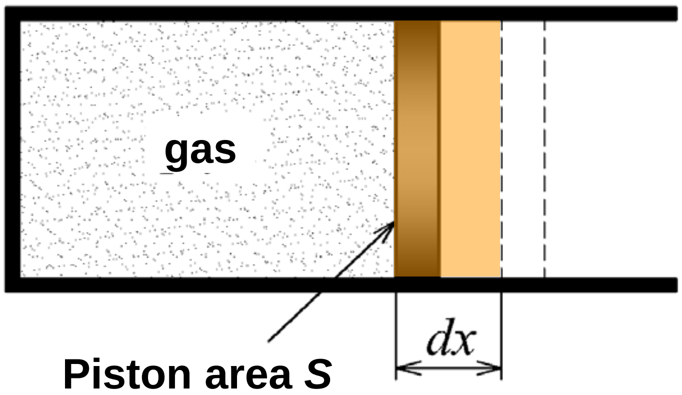
$C_m = 24{,}9\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ for metals $\approx 3R_\mathrm{m}$

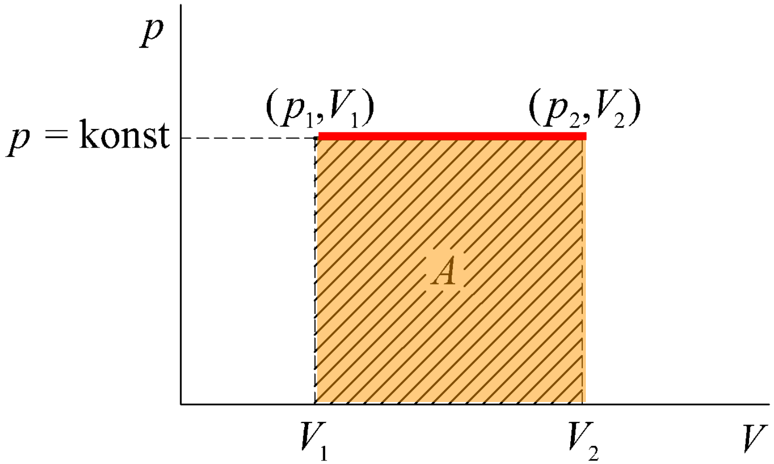
First law of thermodynamics

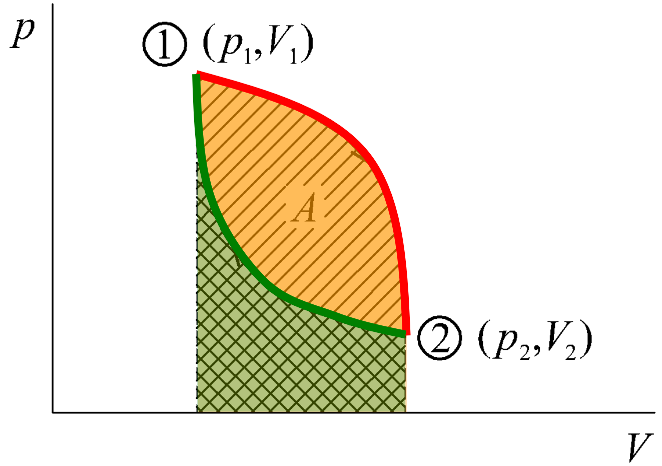
$$dQ = dU + dA$$

perpetual motion machine of the first kind does not exist

A work done by gas







$$dA = F\,dx = pS\,dx = p\,dV$$

heat capacity at constant volume

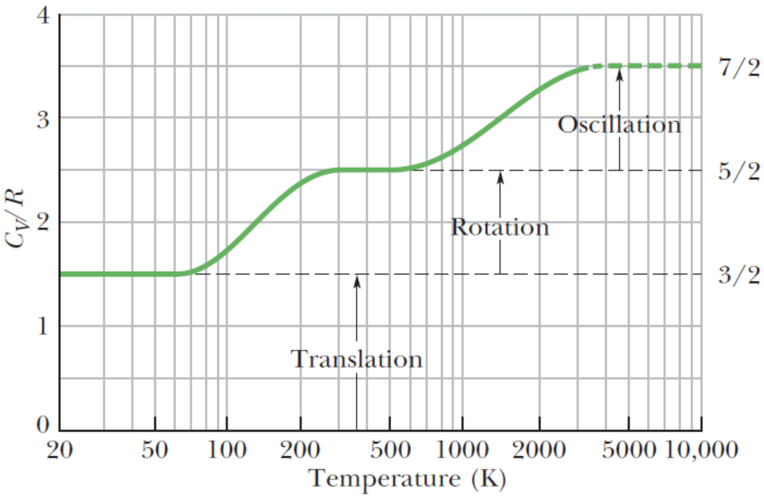
$$C_V = \frac{(dQ)_V}{dT} = \frac{dU}{dT} + \frac{(dA)_V}{dT} = \frac{dU}{dT}$$

$$dU = C_V dT$$

heat capacity at constant pressure

$$C_p = \frac{(dQ)_p}{dT} = \frac{dU}{dT} + \frac{(dA)_p}{dT}$$

$$p\,dV + V\,dp = nR_m dT$$



$$C_p = C_V + nR_m \qquad C_{mp} = C_{mV} + R_m$$

Mayer's relation

$$U = \frac{s}{2} nR_m T \qquad dU = \frac{s}{2} nR_m dT \qquad C_{mV} = \frac{s}{2} R_m \qquad C_{mp} = \frac{(s+2)}{2} R_m$$

Quasistatic processes

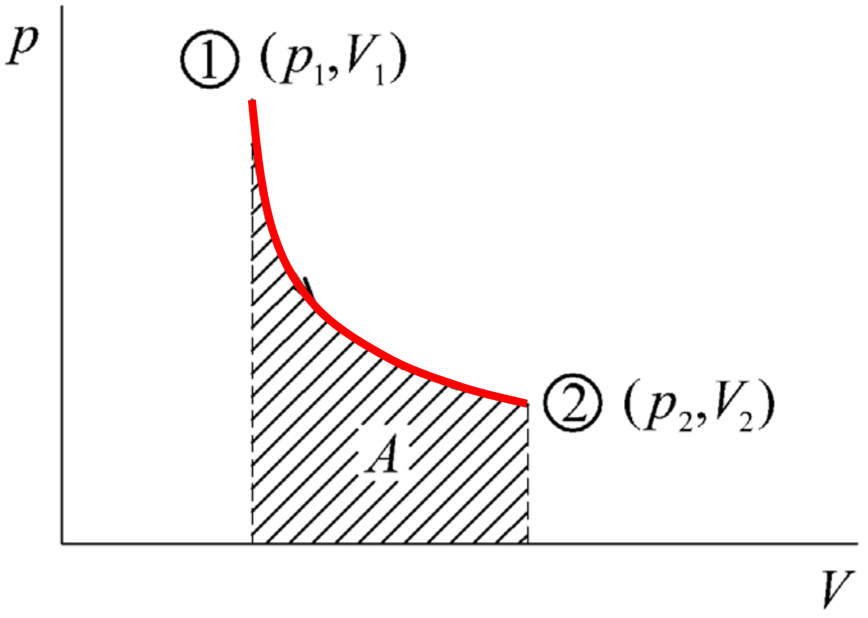
Isothermal process

T = const.

Boyle-Mariotte law

$$pV = nR_mT = konst \qquad dU = 0 \qquad dQ = pdV$$

$$Q = A = \int_1^2 p\,dV = nR_mT\int_1^2 \frac{1}{V}dV = nR_mT\ln\frac{V_2}{V_1} = nR_mT\ln\frac{p_1}{p_2}$$



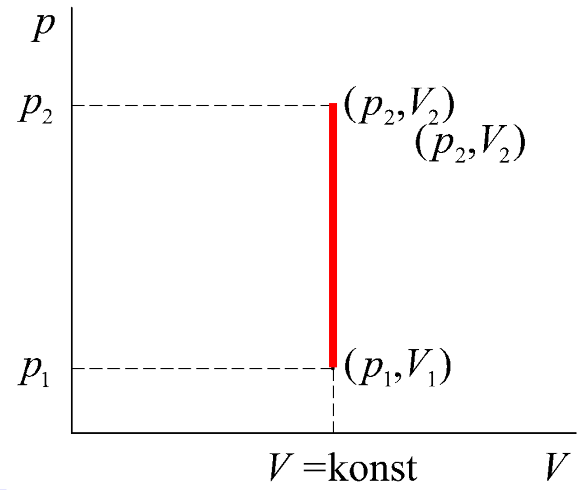
Isochoric process

$V = \text{const.}$

Charles's law

$\frac{p}{T} = \text{const.}$ $\quad pdV = 0 \quad dQ = dU$

$Q = nC_{mV}\Delta T$



Isobaric process

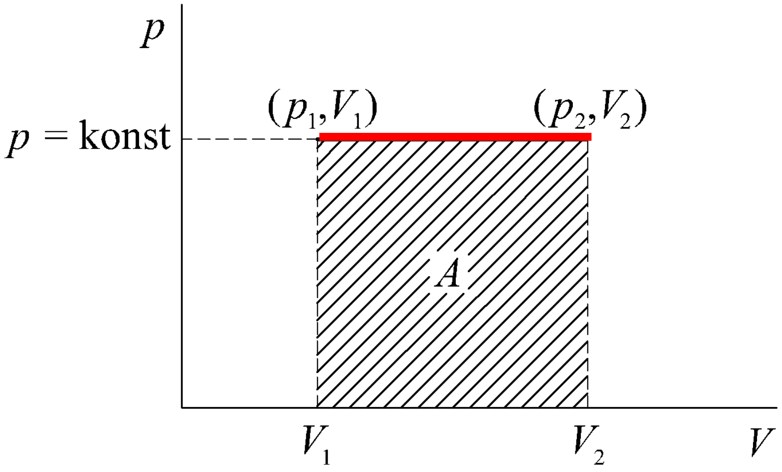
$p = \text{const.}$

$\frac{V}{T} = \text{const.}$

Gay-Lussac's law

$$A = \int_1^2 p\,dV = p\int_1^2 dV = p\left(V_2 - V_1\right)$$

$dQ = dU + pdV \qquad Q = nC_{mp}\Delta T$



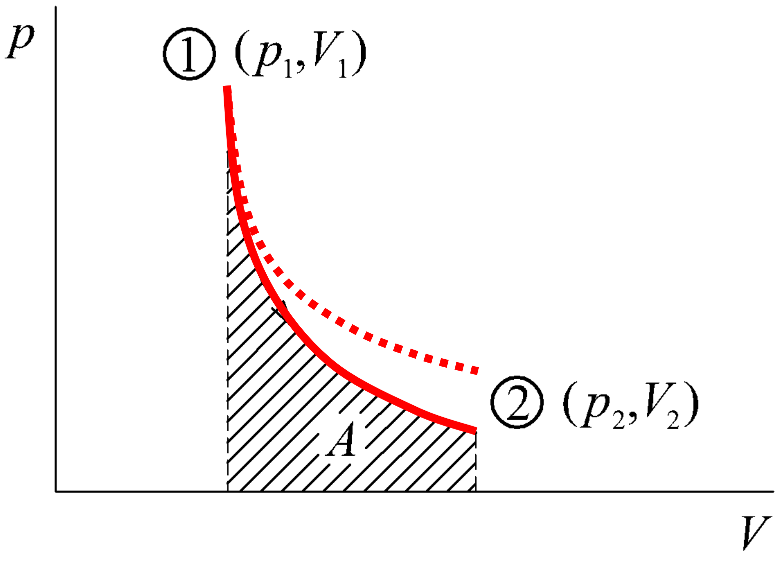
Adiabatic process

$$dQ = 0$$

$$pV^{\kappa} = \text{const.}$$ **Poisson equation** $$\kappa = \frac{C_{mp}}{C_{mV}}$$

$$dA = -dU$$

$$dA = -nC_{mV}\,dT = p\,dV$$



$$ndT = -\frac{p}{C_{mV}}dV$$

$$p\,dV + V\,dp = nR_m\,dT$$

$$ndT = \frac{p\,dV + V\,dp}{C_{mp} - C_{mV}}$$

$$-\frac{p}{C_{mV}}dV = \frac{p\,dV + V\,dp}{C_{mp} - C_{mV}} \Rightarrow \kappa\frac{dV}{V} + \frac{dp}{p} = 0 \Rightarrow \kappa \ln V + \ln p = K$$

$$pV^{\kappa} = \text{const.}$$