Agenda: TD of Dilute Gases, Simple Processes

- Fundamental ideal gas laws,
  - Equations of state (EoS)
  - Isothermal expansion/compression
  - Adiabatic expansion/compression

- Circular processes
  - Work, heat, and entropy in Carnot processes
  - Carnot, Kelvin/Clausius 2ndLTD
  - Thermodynamic driving potentials

- Equation of state of real gases
  - Van der Waals & other models
  - Activity, fugacity
  - Phase equilibria

- Statistical Mechanics
  - Quantum statistics
  - Partition functions

Reading Assignments
Weeks 6 & 7
LN IV.1-4:

Kondepudi Ch. 5.1-5.3, 6.1-6.3.

McQuarrie & Simon
Ch. 2, 5, 6, 7.1-7.4
Math Chapter B, C

Entropy & Energy in Spontaneous Processes

Spontaneous processes = dissipation = equilibration processes are driven by entropy flow $\Delta S > 0$. Reversible processes require $\Delta S \equiv 0$

Microscopic statistical entropy is formulated in terms of actual population probabilities $\{p_i\}$ of Ω accessible configurations (multi-particle states)

$\boxed{S = -N \cdot k_B \cdot \sum_i p_i \cdot Ln\, p_i}$ *N particles* $\boxed{S = -n \cdot R \cdot \sum_i p_i \cdot Ln\, p_i}$ *n moles*

Dilute systems of non-interacting, structure-less, point-like ("ideal") particles

Equation of State $\boxed{P \cdot V = N \cdot k_B \cdot T} \rightarrow \{PVT\}$ *correlation for* *equilibrium states @ max. entropy S*

Internal, equilibrated energy $\boxed{U = N \cdot \frac{3}{2} k_B \cdot T}$ $@T = const.$ See MB, collisions

Process change in internal energy $\rightarrow \boxed{\Delta U = \left(N \cdot \frac{3}{2} k_B\right) \cdot \Delta T = C_V \cdot \Delta T}$

Heat capacity $\boxed{c_V = (3/2) k_B}$ *per particle* $\rightarrow C_V = (3/2) R$ *per mole*

Entropy and Energy State Functions

Spontaneous processes = dissipation = equilibration processes are driven by entropy flow $\Delta S > 0$. Reversible processes require $\Delta S \equiv 0$

$$\text{Processes } (in \to fin):\ \Delta S = S_{fin} - S_{in};\quad \boxed{S(N,V,U=E_{heat}) = k_B \cdot Ln\,\Omega(N,V,U)}$$

$$\text{From earlier } \to \Omega(N,V,U=E_{heat}) \propto V \to \text{ and } \boxed{E_{heat} \triangleq U = T \cdot S}$$

$$\boxed{\left(\frac{\partial S(N,V,U)}{\partial U}\right)_{N,V=const} = \frac{1}{T}}$$

$$\text{Distributed total energy } U \to \frac{U}{N} = E_{heat} = k_B \cdot T$$

$$\left(\frac{\partial S(N,V,U)}{\partial V}\right)_{N,U} = k_B \cdot \left(\frac{\partial Ln[\Omega(\ldots)]}{\partial V}\right)_{N,U} = ?$$

Use again $\Omega(N,V,U) \propto V$

$$k_B\left(\frac{\partial Ln V}{\partial V}\right)_{N,U=const} = \frac{k_B}{V} = (EoS) = \frac{P}{T}$$

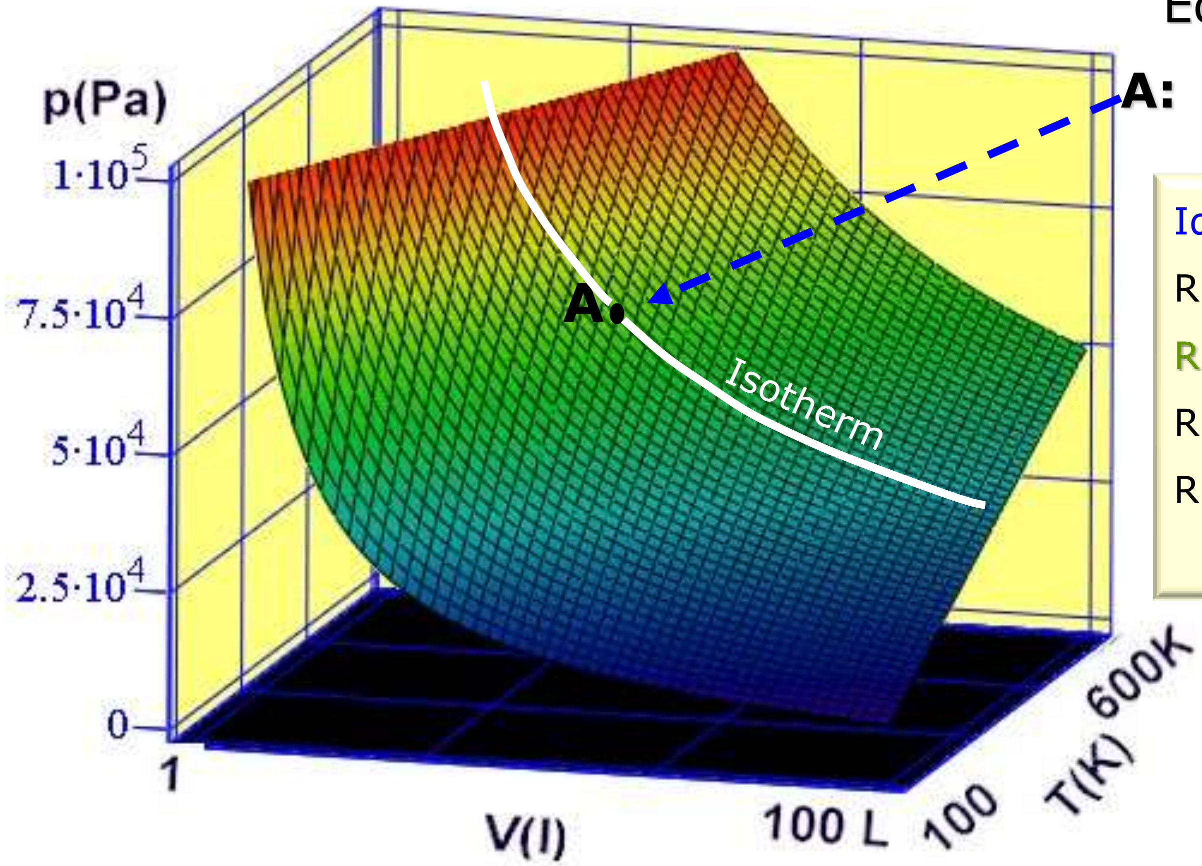
$$\boxed{dS = \underbrace{\frac{1}{T} \cdot dU}_{\text{Heat}} + \underbrace{\frac{P}{T} \cdot dV}_{\text{P-V work}} - \underbrace{\frac{\mu}{T} \cdot dN}_{\text{Chemical}}} \Rightarrow \boxed{S(U,V,N) = k_B \cdot Ln\,\Omega = \frac{1}{T} \cdot U + \frac{P}{T} \cdot V - \frac{\mu}{T} \cdot N}$$

The (Ideal-Gas) Equation of State

$p \cdot V = n \cdot R \cdot T$; n=# moles, T → U

Non-interacting → Only gas phase!

Hyperplane of Equilibrium States



A: p(V,T)= n·R·T/V

Ideal Gas Constant *R*

R = 0.0821 liter·atm/mol·K

R = 8.3145 J/mol·K

R = 8.2057 m^3·atm/mol·K

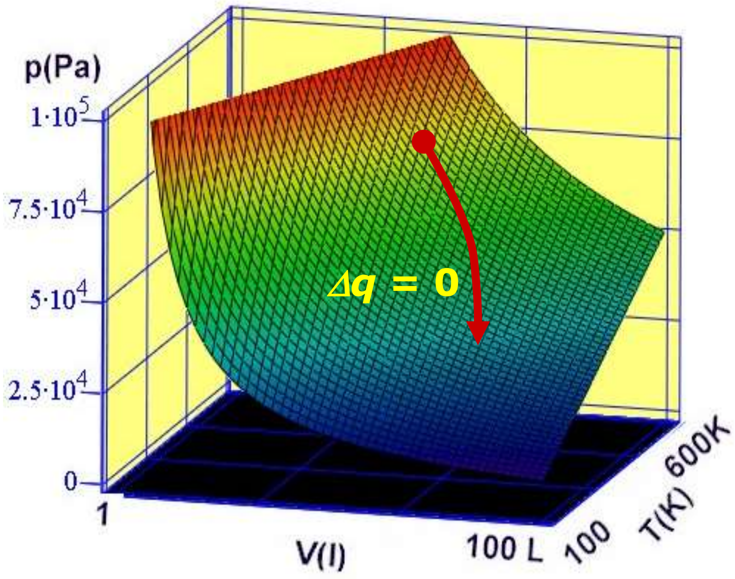
R = 62.3637 L·Torr/mol·K or

L·mmHg/mol·

State functions p, V, T,… . Molar ***p*(V,T)** hyper-plane (monotonic) contains all possible gas states ***A***. There are no other states of the gas.

The Adiabatic Equation of State

$p\cdot V = n\cdot R\cdot T$; n=# moles, $T \rightarrow U$
Non-interacting → Only gas phase!



EoS+1^{st}LTD→Relation between internal energy of ideal gas and pressure-volume relation.

Adiabatic expansion means (here) no exchange of heat energy, d*q*=0.

Calculation for 1 *mole ideal gas*

$dU = dq - pdV$ and $dq = 0 \rightarrow$

$$0 = dq = dU + p\cdot dV \rightarrow dU = -p\cdot dV < 0$$

$$\boxed{dU\left(V,T\right) = C_V\cdot dT < 0}$$

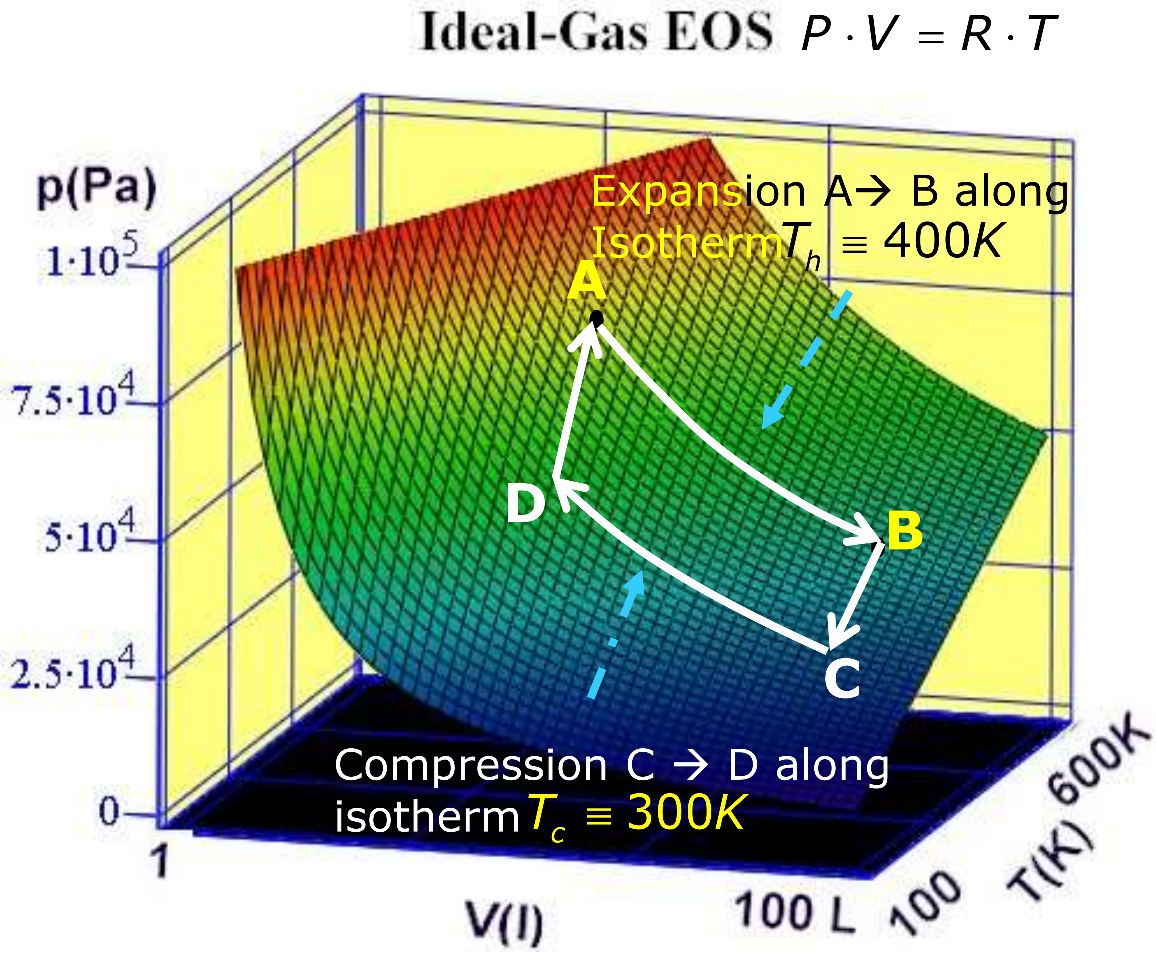
$$0 = C_V\cdot dT + p\cdot dV = C_V\cdot dT + \frac{R\cdot T}{V}\cdot dV$$

$$C_V\cdot\frac{dT}{T} + R\frac{dV}{V} = 0 \rightarrow \frac{dT}{T} + \left(\frac{R}{C_V}\right)\frac{dV}{V} = 0$$

Later : $C_P = C_V + R;\quad \gamma := c_P/c_V$

$$\boxed{\frac{dT}{T} + \left(\gamma - 1\right)\frac{dV}{V} = 0} \Rightarrow \boxed{\begin{aligned} T\cdot V^{\gamma-1} &= const.\\ p\cdot V^{\gamma} &= const.\\ T^{\gamma}\cdot p^{1-\gamma} &= const.\end{aligned}}$$

Circular Processes on EoS Hyperplane

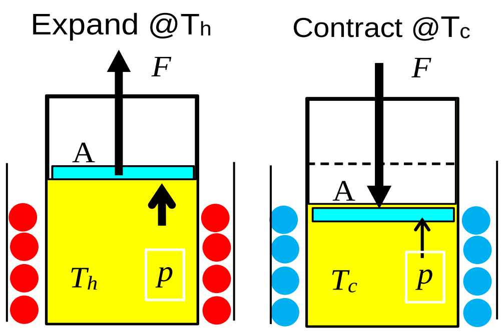


$P \cdot V = R \cdot T$

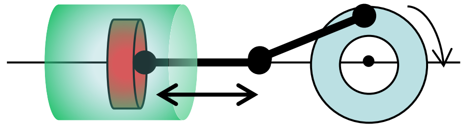
Expansion A→ B along Isotherm $T_h \equiv 400K$

Compression C → D along isotherm $T_c \equiv 300K$

A circular process
A→B→C→D→A
on the EoS hyperplane



Heating $\boldsymbol{T}_h > \boldsymbol{T}_c$ *Cooling*



returns the IG system to its initial state A after a combination of slow (=reversible) expansion and compression processes.

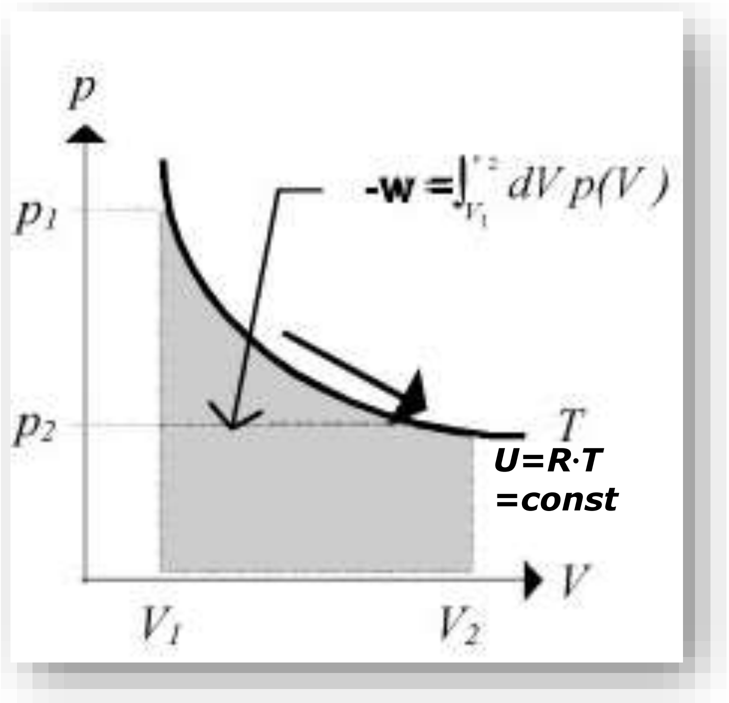
Ideal Gas Constant *R*

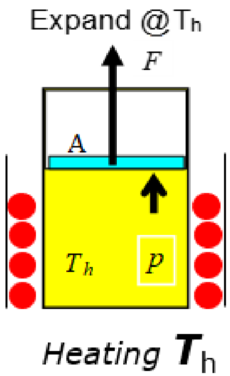
R = 0.0821 liter·atm/mol·K

R = 8.3145 J/mol·K

Heat and cool the working IG volume @ specific times → Cyclic thermal engine

Isothermal Expansion/Compression





w = - area under curve *P*(V) (1 mole)
Total expansion work ($V_1 \rightarrow V_2$) reduces internal energy (cools):

Use $p\cdot V = R\cdot T$ *for expanding* 1 *mole*

$$w = -\int_{V_1}^{V_2} p(V)\,dV = -R\cdot T\int_{V_1}^{V_2}\frac{dV}{V} =$$

$$= -R\cdot T\cdot\ln\left(\frac{V_2}{V_1}\right) < 0$$

$w < 0$ *implies system does work on environment*

on surroundings

But $\Delta U \propto \Delta T = 0 \rightarrow q > 0$ (*must absorb heat*)

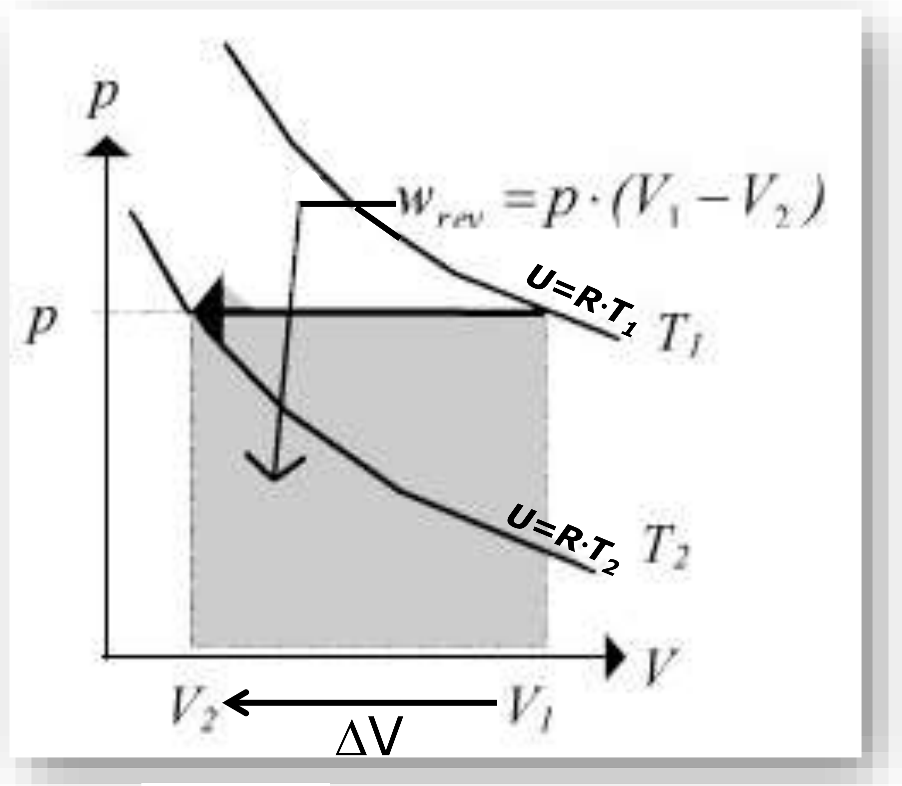
$\underline{1.\ LTD:}$

$$\rightarrow q = \underset{=0}{\Delta U} - w = -w = R\cdot T\cdot\ln\left(\frac{V_2}{V_1}\right) > 0$$

absorbed @T

Isobaric Compression

Compress 1 mole at *p=const.*



Work done on system @ $p = const.$:

$$w = -\int_1^2 p(V)dV = -p\cdot\int_1^2 dV > \mathbf{0}$$

$$= -p\cdot\Delta V = -R\cdot\Delta T = \text{Shaded Area}$$

$$\rightarrow \text{tends to increase } U, T$$

But at $p = const.\ T_1 \rightarrow T_2 < T_1$

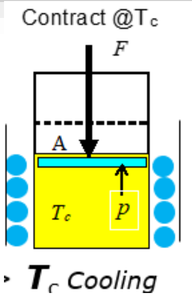
Internal energy change

$$\Delta U = q + w \overset{!}{=} C_V\cdot[T_2 - T_1] < 0$$

$$q = \Delta U - w = \Delta\left(U + p\cdot V\right)_P$$

$$q = \Delta H = \left(C_V + R\right)\cdot[T_2 - T_1]$$

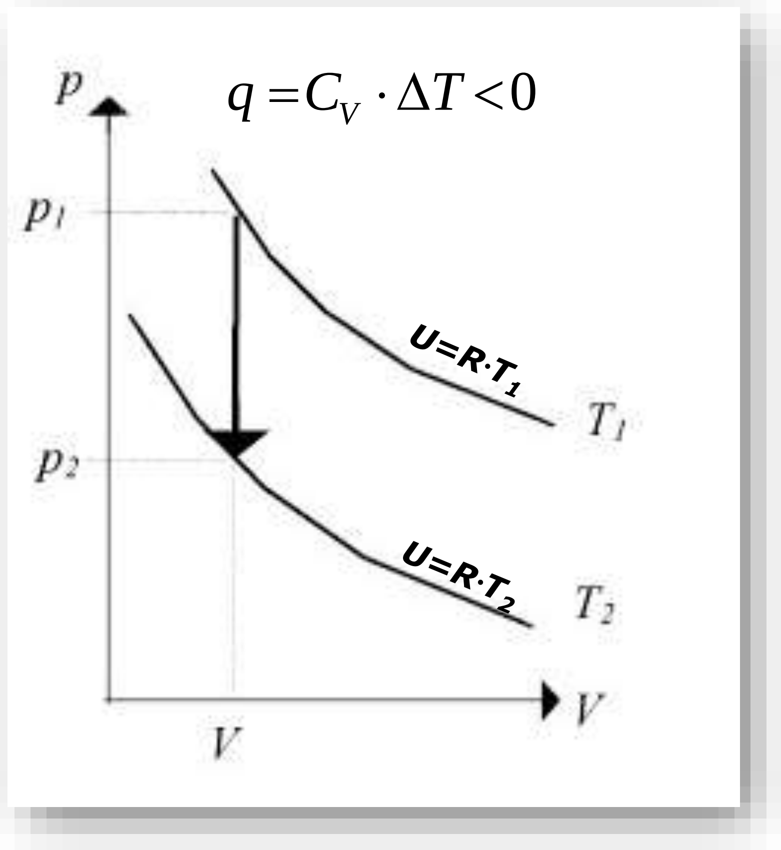
Cool gas ! $q = C_p\cdot\Delta T = \frac{5}{2}R\cdot\Delta T < \mathbf{0}$



Enthalpy change (for $p = const.$) : $\Delta H = C_p\cdot\Delta T \rightarrow C_p = C_V + R$

Inverse process: heating at constant *p*, e.g., *p=p*$p=p_{atm}$, *leads to expansion,* $V_2 \rightarrow V_1 > V_2 \rightarrow$ *drives piston out.*

Isochoric Decompression



Isochoric (V = const.) decompression
→ of 1 mole w =-pΔV=0

No work done on system $w = 0$

But $\Delta U < 0, \rightarrow$ *system must emit heat*

$$q = C_V \cdot \Delta T = C_V \cdot [T_2 - T_1]$$

1. *Law of Thermodynamics :*

$$\Delta U = q + w = q = C_V \cdot [T_2 - T_1] < 0$$

Enthalpy change

$$\Delta H = \Delta U + \Delta(p \cdot V) = (C_V + R) \cdot \Delta T$$

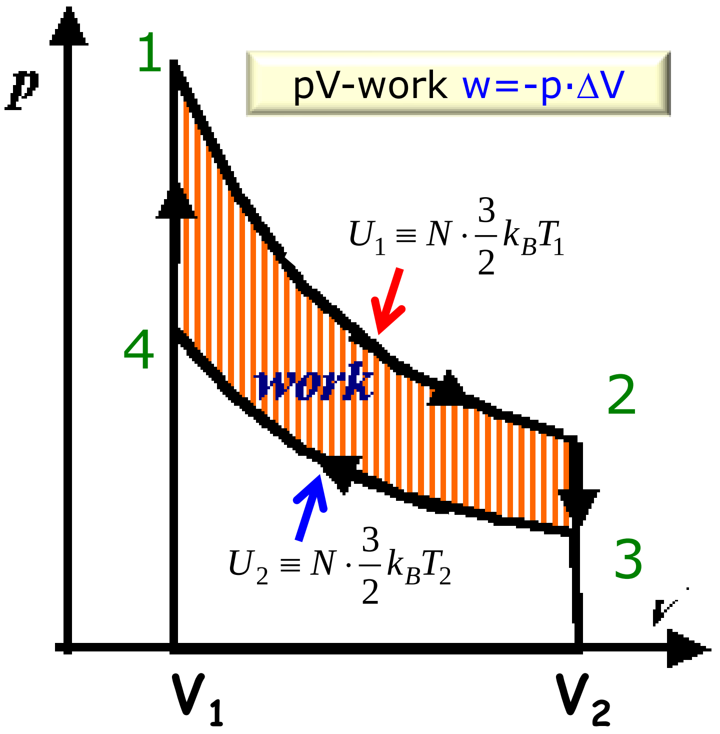
$$= C_p \cdot [T_2 - T_1] \quad (always = C_p \cdot \Delta T)$$

$NOTE : \Delta H \neq q \; (since \;\; p \neq const)$

Inverse process: heating at constant *V*, leads to increased temperature and pressure.

Thermal Engine: Expansion-Compression Cycles

Ideal-gas system (N particles) absorbing external heat *(q>0)* can produce mechanical work *(w<0)* on surroundings. Continuous operation requires cyclic process (in p-V-T).
→ Needs good contacts to heat bath @T_1 and heat sink @T_2 → reversible processes



pV-work $w=-p\cdot\Delta V$

In one cycle the gas absorbs net heat energy and does the net work,

$w = w_1 + w_2 = -q = C_V\cdot[T_2-T_1]$

Not all absorbed heat is converted, some must be dumped as waste heat.

1) Isothermal expansion at T_1=const.
2) Isochoric decompression at V_2=const.,
3) Isothermal compression at T_2 =const.
4) Isochoric compression V_1=const.,

Sign convention: Internal energy gain or loss

→ **Work-Heat Balance:**

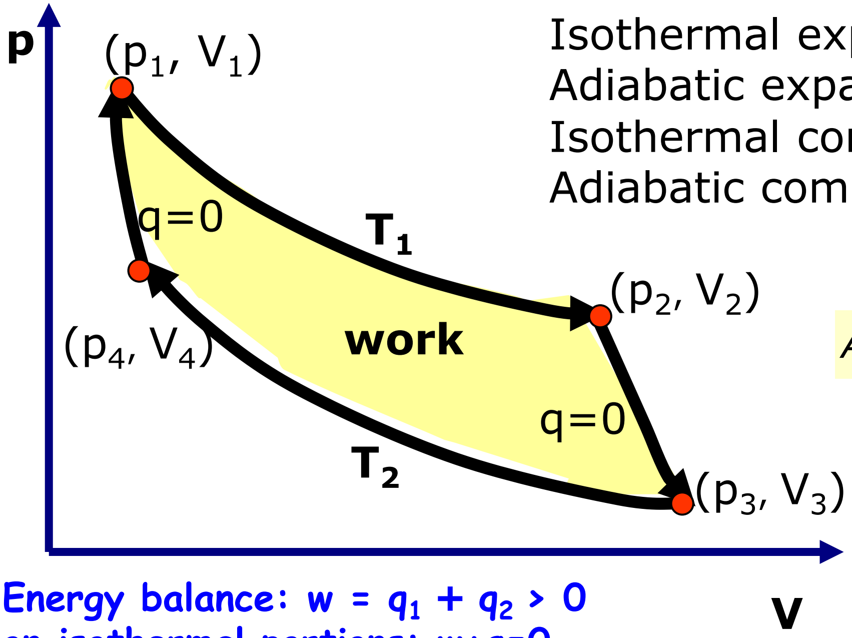
1-2 gas does work	$-w_1 = q_1$;	$\Delta U = 0$
2-3 gas is cooled	$q < 0$;	$\Delta U < 0$
3-4 gas is compressed	$w_2 = - q_2$;	$\Delta U = 0$
4-1 gas is heated	$q > 0$;	$\Delta U > 0$

Total internal energy: **$\Delta U = 0$ (cyclic)**

Total heat absorbed: **$q = q_1+q_2=-w > 0$**

Total work by engine : **$w = w_1+ w_2 < 0$**

Carnot Engine Cycles



Isothermal expansion at $T_h=T_1$
Adiabatic expansion $T_h \rightarrow T_c=T_2$
Isothermal compression at $T_c=T_2 < T_h$
Adiabatic compression $T_c \rightarrow T_h=T_1$

Adiabatic $(q=0)$ *EoS* $\boxed{T \cdot V^{\gamma-1} = const}$ $\gamma = c_p/c_V$

Adiab. expansion/compr. → $V_4/V_1 = V_3/V_2$
→ $V_2/V_1 = V_3/V_4$

Energy balance: $w = q_1 + q_2 > 0$
on isothermal portions: $w+q=0$
Adiabatic works cancel

$$\boxed{q_1} = -w_1 = \int_{V_1}^{V_2} \underbrace{p}_{=RT_1/V} \; dV = R \cdot \boxed{T_1} \cdot \ln\left(\frac{V_2}{V_1}\right) > 0$$

$$\boxed{q_2} = -w_2 = \int_{V_3}^{V_4} p \cdot dV = -R \cdot \boxed{T_2} \cdot \ln\left(\frac{V_3}{V_4}\right) < 0$$

$$\text{"}Entropy\text{"} \quad \boxed{\frac{q_1}{T_1} = -\frac{q_2}{T_2}} = -\Delta S_2 = \Delta S_1$$

Entropy is conserved in reversible cyclic processes: $\Delta S_1 + \Delta S_2 = 0.$

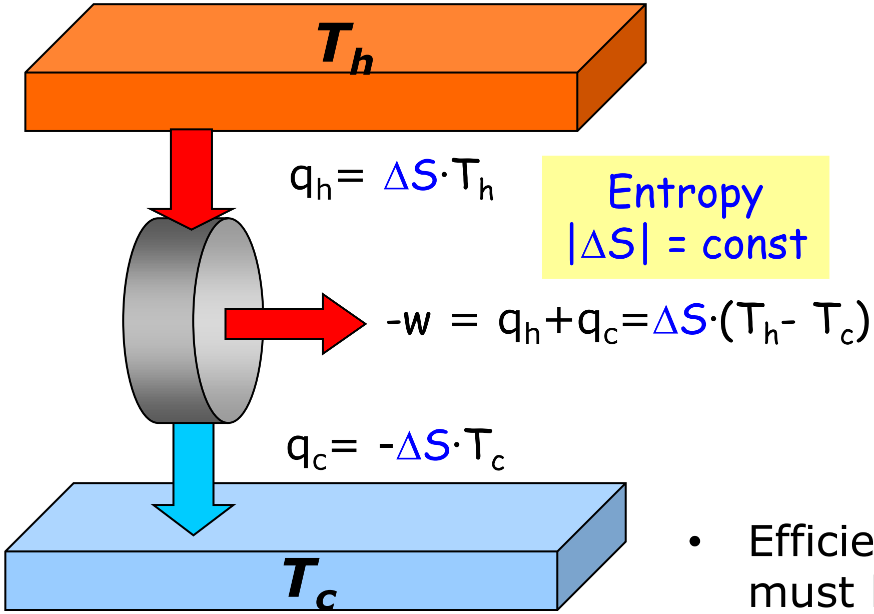
$$\boxed{\rightarrow S = state \;\; function \; (descriptor)}$$

For any process: $\Delta S_{A \rightarrow B} \geq \dfrac{q_{A \rightarrow B}}{T}$

$=$ *sign for reversible* $A \rightarrow B$ *only.*

Reversible adiabatic exp./compr.: $\Delta S = q/T = 0$ since $q = 0$.
Irreversible adiabatic exp./compr.: $\Delta S \neq 0$.

Efficiency of Carnot Engines



$q_h = \Delta S \cdot T_h$

Entropy
$|\Delta S| = const$

$-w = q_h + q_c = \Delta S \cdot (T_h - T_c)$

$q_c = -\Delta S \cdot T_c$

Efficiency of an ideal Carnot engine

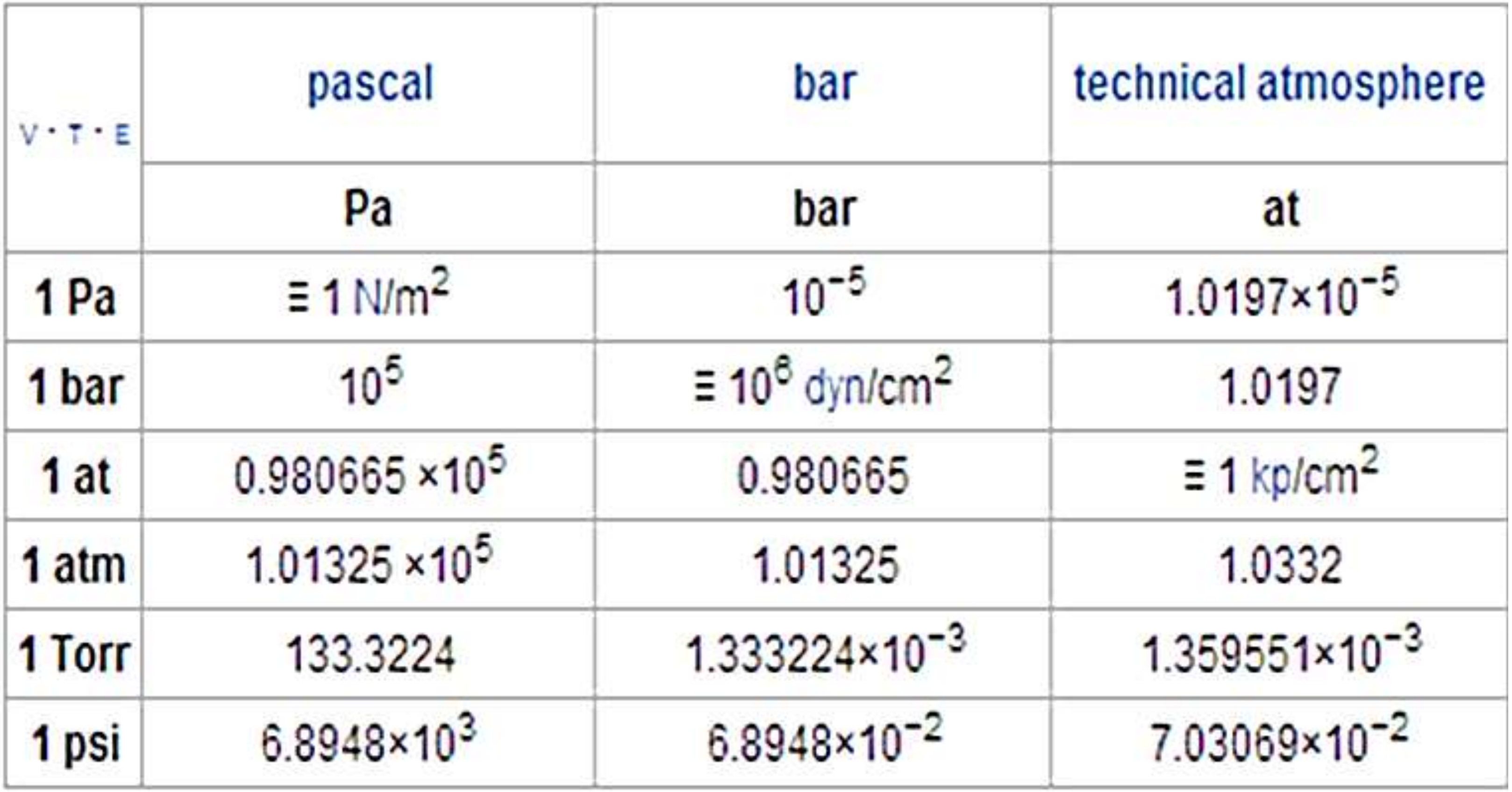
$$\varepsilon_C = \frac{-w}{q_h} = \frac{q_h + q_c}{q_h}$$

$$\varepsilon_C = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \xrightarrow[T_h \to \infty]{} 1$$

- Efficiency of a realistic Carnot-type engine must be lower than ε_C.
- All engines based on *pV* processes can be simulated by a combination of Carnot processes.
- No thermodynamic (*pV*) engine can have an efficiency larger than ε_C.

Typical thermal engines have efficiencies of $\boxed{\varepsilon_{therm} \sim 0.3}$.

Pressure Units



V · T · E	pascal	bar	technical atmosphere
	Pa	bar	at
1 Pa	$\equiv 1$ N/m^2	10^{-5}	1.0197×10^{-5}
1 bar	10^5	$\equiv 10^6$ dyn/cm^2	1.0197
1 at	0.980665×10^5	0.980665	$\equiv 1$ kp/cm^2
1 atm	1.01325×10^5	1.01325	1.0332
1 Torr	133.3224	1.333224×10^{-3}	1.359551×10^{-3}
1 psi	6.8948×10^3	6.8948×10^{-2}	7.03069×10^{-2}