Agenda: Kinetics and Transport in Multiparticle Systems

Dynamics of interacting multi-particle systems

- Interaction energies
  Dissipation via multiple scattering
- Probabilistic evolution
  Random walk and binomial distribution
  Diffusion processes
  Maxwell-Boltzmann energy distributions
  Fluctuating (Langevin) dissipative forces
- Kinetics of dilute gases
  Work and heat transfer
    Flow of heat and radiation
    Laws of thermodynamics, thermodynamic ensembles, entropy
- Fundamental ideal gas laws, Equation of state (EoS)

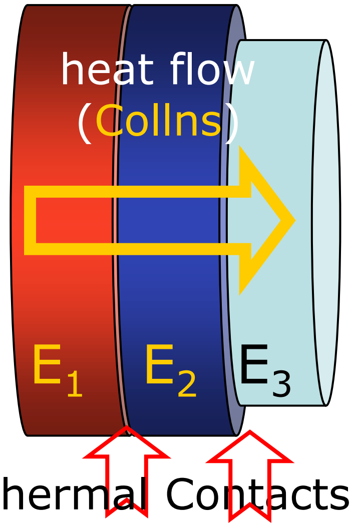
Reading Assignments
Weeks 5 & 6
LN IV.1-4:

Kondepudi Ch. 1-3.
Additional Material

McQuarrie & Simon
Ch. 2, 5
Math Chapter B, C

Energy Equilibration By Heat Exchange

Composite System
CS=Sys$_1$ Sys$_2$



Constant energy $\boldsymbol{E}=E_1+E_2+E_3$ → Search for the most likely final energy partition $E_1/E_2/E_3$. For each spontaneous exchange of heat $-\Delta q_1=\Delta E_2+\Delta E_3$ → increase exc. P_{CS}

Equilibrium partition $\{E_1,\ldots,E_n\}$ *maximizes excited* Ω_{CS}

$$\frac{1}{\Omega_n}\frac{d\Omega_n(E_n)}{dE_n} = const.\ function\ \left(E=\sum_n E_n\right)$$

dimension $[\ ]$ $=1/Energy$

Plausible Ansatz:

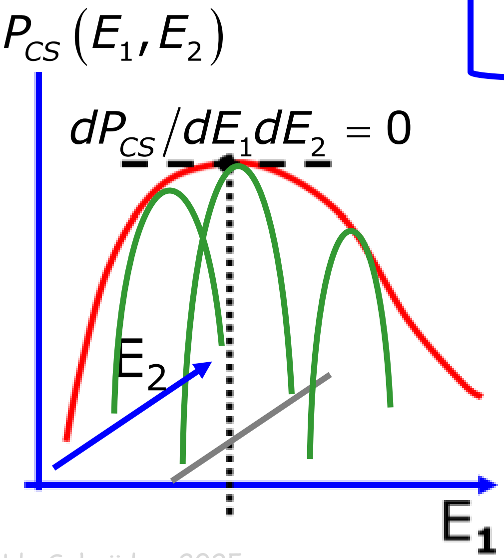
$$\frac{d}{dE}\underbrace{Ln\,\Omega_{CS}(E)} = const.\left(\langle E\rangle\right) \propto \frac{1}{k\cdot T}$$

$$dS(E)/k \propto \frac{dE}{k\cdot T}$$

*Def.=***S/k** → **Entropy** =*deg. disorganization*

$$\boxed{dE = T\cdot dS}$$

$$dS = \frac{dq}{T} = \frac{Spont.\ Heat\ Transfer}{Temperature}$$



Spontaneous energy redistribution requires entropy increase $\Delta S>0$ (opposite is not true!)

Entropy and Energy at Equilibrium

Spontaneous equilibration of systems in thermal contact →

$$\boxed{\frac{d}{dE} Ln\Omega(E,N) = \frac{dS(E,N)}{dE} = \underline{\underline{Const}}\left(E,N\right)}$$

Dimension [Const(*E*,*N*)]= 1/energy.

Material & size independence → **Const(E,N) = Intensive function**
(like <*E*>) depends on total energy *E* supplied as heat & total number of particles.

Obvious *intensive energy* variables: Mean energy per particle ~ temperature ***T***

Previously: energy content of system of *N* independent particles: $\boxed{\langle E\rangle_N = E/N \triangleq k_B \cdot T}$

$$\boxed{Adopt\ intensive\ Const.(E,N)\ with\ \frac{dS}{dE} = \frac{d}{dE} k_B \cdot Ln\Omega(E) \propto \frac{1}{T}}$$

=Simplest form compatible
S extensive

$$S(E) = k_B Ln\ \Omega = \cancel{S_0} + \frac{E}{T} \rightarrow \boxed{\left.\begin{matrix} Distributed \\ heat\ energy \end{matrix}\right\} E = \Delta q = T \cdot S}$$

Set integration constant =0

Entropy and Energy at Equilibrium

Spontaneous equilibration of systems in thermal contact

$$\boxed{\frac{d}{dE} Ln\Omega(E,N) = \frac{dS(E,N)}{dE} = \underline{\underline{Const}}\left(E,N\right)}$$

E_{heat}

Dimension [Const(*E*,*N*)]= 1/energy.

$$Function\ Const(E,N) = \frac{dS}{dE} = \frac{d}{dE} k_B \cdot Ln\,\Omega(E) \propto \frac{1}{T}$$

Simplest *E*-dependence compatible

$$\boxed{S(E_{heat},N) = k_B \cdot Ln\ \Omega_N(E_{heat})} = \frac{E_{heat}}{T}\ \ with\ S_0 = S\left(0\right) := 0$$

$Since\ \Omega_{1+2} = \Omega_1 \cdot \Omega_2$ and $Ln\ \Omega_{1+2} = Ln\Omega_1 + Ln\Omega_2$ Entropy ***S*** scales with size → *S extensive*

Spontaneous heat *re – distribution @T*	$: \Delta\langle E\rangle = \Delta q \to \boxed{\Delta S = \frac{\Delta q}{T} > 0}$

Distributed heat energy $\boxed{E = T \cdot S}$

$$\boxed{\Delta S = S_{fin} - S_{in} = k_B \cdot Ln\left(\frac{\Omega_{fin}}{\Omega_{in}}\right)}$$

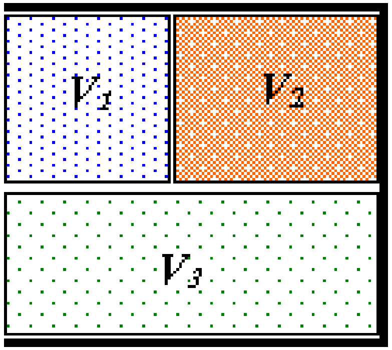
$\Omega = populated\ (excited)$

configurations (conformations)

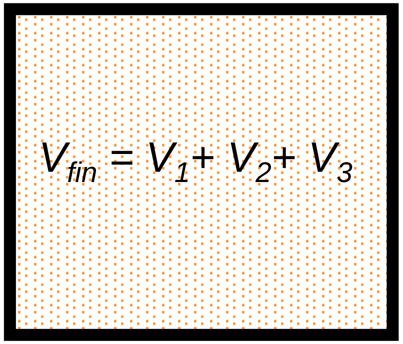
Equilibration processes are driven by entropy flow ΔS > 0

Example: Entropy Gain in Spontaneous Gas Mixing

In: Separated Gases



Fin: Mixed Gases



$$V_{fin} = V_1 + V_2 + V_3$$

S - gain by individual gas components $\rightarrow \boxed{\Omega_i \propto V_i \ volume}$

Entropy is extensive (*additive*). →*conponents add*

$$\boxed{S_i = n_i \cdot R \cdot Ln\left(V_i / \upsilon\right) > 0}$$

$n_i =$ *number of moles i*

$\upsilon =$ *scale*

$$Gas\ const.\ R = 6.022 \cdot 10^{23} \cdot k_B = 8.31 J/mol$$

Initial *Final*

$$S_{in} = R \cdot \sum_i n_i \cdot Ln\left(V_i/\upsilon\right) \Rightarrow S_{fin} = R \cdot Ln\left(V_{fin}/\upsilon\right) \cdot \sum_i n_i$$

$$\boxed{\Delta S = -R \cdot \sum_i n_i \cdot Ln\left(\frac{V_i}{V_{fin}}\right) > 0}$$

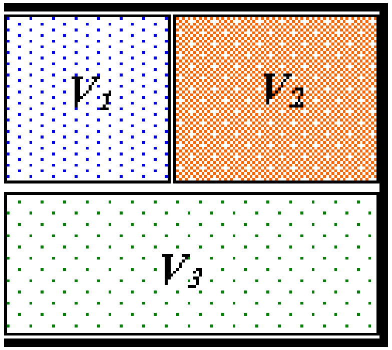
Spontaneous ↗

No heat exchange

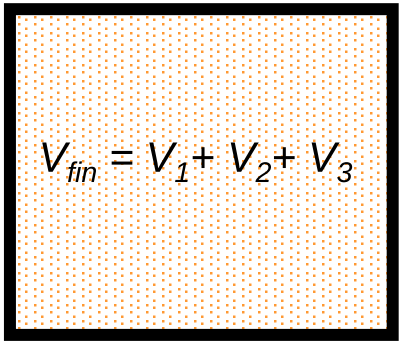
$$Total\ \#moles\ n = n = \sum_i n_i;\ total\ vol\ V = \sum_i V_i$$

Formulation Gain in Microscopic Entropy Notation

In: Separated Gases



Fin: Mixed Gases



$$V_{fin} = V_1 + V_2 + V_3$$

$$\boxed{\Delta S = -R \cdot \sum_i n_i \cdot Ln\left(\frac{V_i}{V_{fin}}\right) > 0}$$

Spontaneous ↗

No heat exchange

$$Total\ \#moles\ n = \sum_i n_i;\quad total\ volume\ \ V = \sum_i V_i$$

$$\Delta S = -n \cdot R \cdot \sum_i \left(\frac{n_i}{n}\right) \cdot Ln\left(\frac{V_i}{V}\right)$$

Relative abundance (population probability)

for particle type i $\rightarrow p_i = \frac{n_i}{n} = \frac{V_i}{V} < 1$

$$\boxed{\Delta S = -n \cdot R \cdot \sum_i p_i \cdot Ln\, p_i}$$

n moles

$$\boxed{\Delta S = -N \cdot k_B \cdot \sum_i p_i \cdot Ln\, p_i}$$

N particles

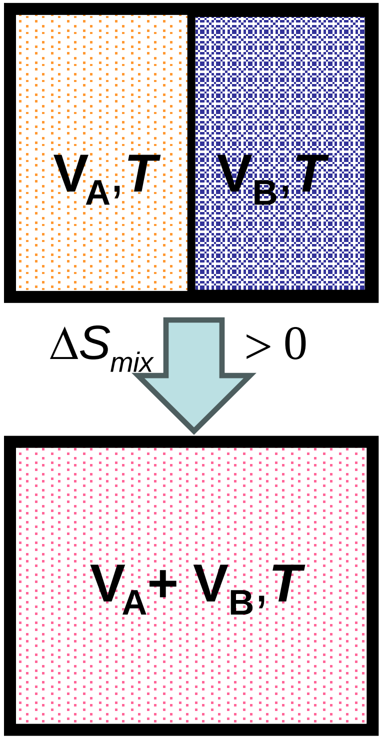
Entropy of Mixing: Example

One mole each of two equivalent ideal gases, ***A=O$_2$*** and ***B=H$_2$***, in their respective halves of a separated container at ***$P_A = P_B = 1atm$***, ***$T_A = T_B = 298K$***

s.p. spaces $\varpi_A \propto V_A$ and $\varpi_B \propto V_B$

When partition is removed, the gases will mix.

No change in energy
$\Delta q = 0$



Total *$n = 2$ moles* ; Mole fractions: $n_A/n = n_B/n = 0.5$.
→ probabilities are $p_A = p_B = 0.5$ *also in state space*

→ "Entropy of Mixing"

$$\Delta S_{mix} = -nR\left\{\frac{n_A}{n}\cdot Ln\left(\frac{n_A}{n}\right)+\frac{n_B}{n}\cdot Ln\left(\frac{n_B}{n}\right)\right\} =$$
$$= -2R\left\{0.5\cdot Ln(0.5)+0.5\cdot Ln(0.5)\right\} = 11.5\,J/mol\cdot K > 0$$

Entropy is gained ←→ mixing occurs spontaneously.

$$\Delta S = \frac{\Delta q}{T} \text{ or } \Delta S > \frac{\Delta q}{T} \text{ in spontaneous processes}$$

Universal Gas Constant
R=8.31*J/mol·K*

Mixed gases are difficult to unmix (costs energy)!

Entropy Flow in Spontaneous Processes

$$\Delta S = \frac{\Delta q}{T} \; or \; \Delta S > \frac{\Delta q}{T} \; in\ spontaneous\ processes$$

$$\boxed{\Delta S \geq \frac{\Delta q}{T}}$$

Equilibration processes are driven by entropy flow $\Delta S > 0$

Equilibrated systems are at maximum entropy.
Their evolution does not rely on entropy flow → $\Delta S \equiv 0$
Processes connecting equilibrated systems are reversible.

Thermodynamic Energies & Driving Potentials

Internal structural energy of 1mole material :

extensive (additive) state function U

Enthalpy Structural Energy plus pressure – volume work

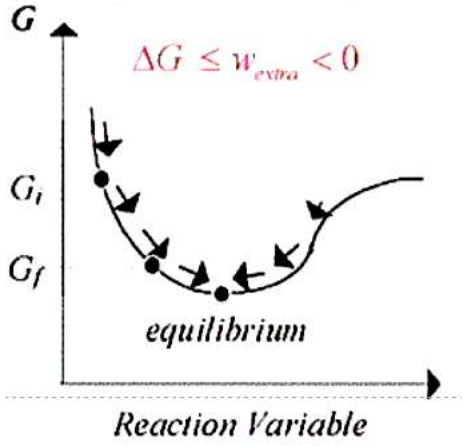
extensive state function $H = U + P \cdot V \rightarrow \Delta H\big|_p = \Delta U + p \cdot dV$

$$\text{Example}\ \ comp(reag1 + reag2) \rightarrow\ H_{comp} = H_{reag1} + H_{reag2} + \Delta H_{rxn}$$

Reference energy H^0 @ *standard state* $T = 25^0 C,\ P = 1bar \leftarrow$ *large databases*

$H^0 = 0$ *for pure elemental substances (incl phase)*

Energy gain per product mole in reaction $\boxed{\Delta H^0_{rxn} = H^0_{products} - H^0_{reagents}}$



Helmholtz free energy $A = U - T \cdot S$ *used @ const* V, T

System will do spontaneously : $w_{process} = \Delta A_{process} < 0$

Gibbs free energy $G = H - T \cdot S$ *used @ const* p, T

System will do spontaneously : $w_{process} = \Delta G_{process} < 0$

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
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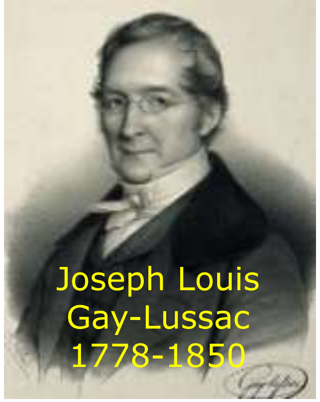
Thermodynamics: Ideal-Gas Equations of State EoS


Robert Boyle
1627-1691


Guillaume
Amontons
1663-1705


Joseph Louis
Gay-Lussac
1778-1850

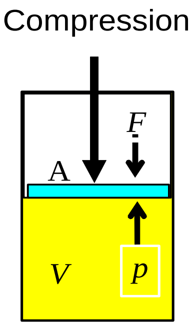
Robert Boyle, Guillaume Amontons, Gay-Lussac, Dalton,..

Response of dilute gases of specified amounts (#moles = *n, Avogadro*)

Boyle's Law $P(V) \propto 1/V$ or $\boxed{P \cdot V = const(n,T)}$

Amontons' (Gay – Lussac's) Law $\boxed{P(T) = P(0) \cdot \left[1 + \alpha \cdot T_C\right] \propto T}$

Charles' Law $V(T_C) = V(0^0 C) \cdot \left[1 + \alpha \cdot T_C\right] \rightarrow \boxed{V(T) \propto T}$ *(Kelvin)*



$\alpha \approx 3.66 \cdot 10^{-3}/{}^0C \approx 1/273{}^0C$ → absolute temperature *T*

EoS of Ideal Gases

Isentropic *T*=const. $\boxed{P \cdot V = n \cdot R \cdot T = N \cdot k_B \cdot T}$

Polytropic EoS

Polytrope coefficient $\gamma = C_P / C_V$

$$\boxed{\begin{array}{l} P \cdot V^{\gamma} = const; \\ T \cdot V^{\gamma - 1} = const \end{array}}$$

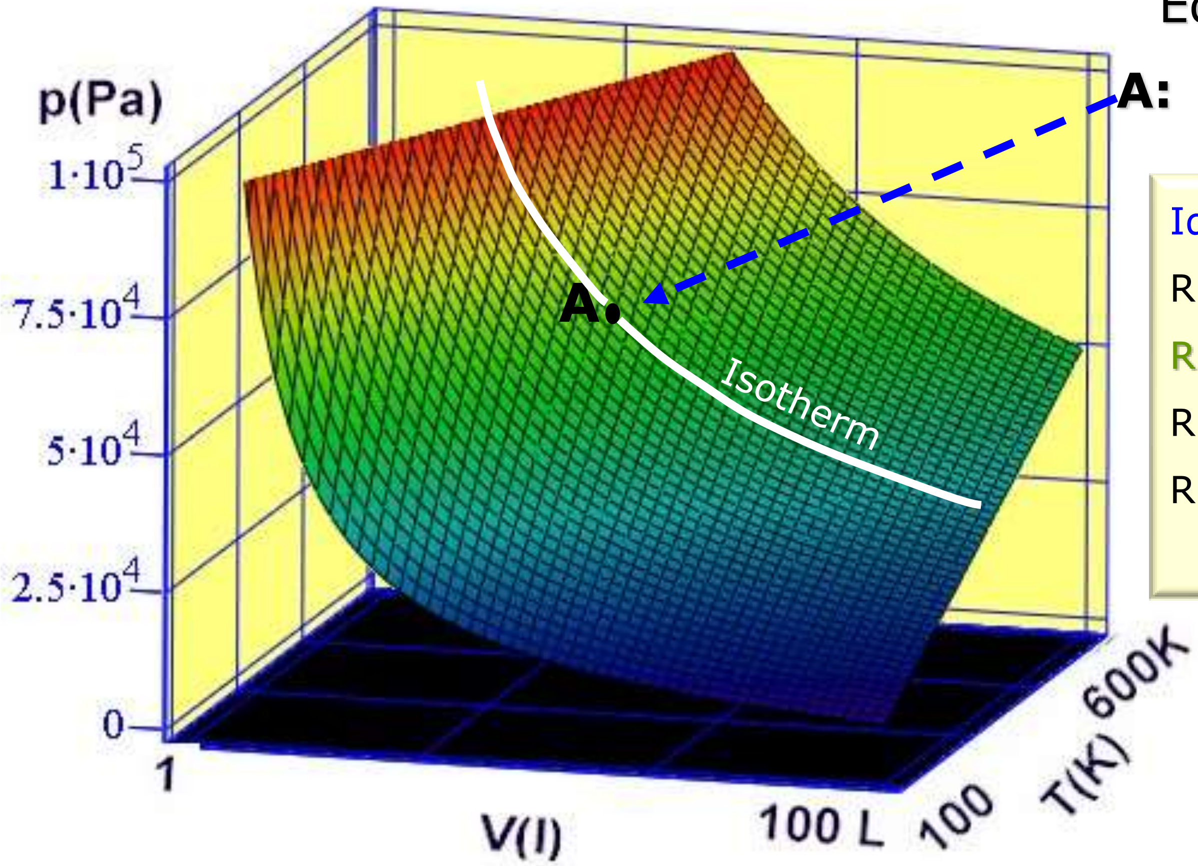
2 Specific Heats $@\, P = const.$ *or* $V = const.$

Thermal energy content $\boxed{Q = C_{P,V} \cdot T}$ *Empirical Law*

The (Ideal-Gas) Equation of State

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

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

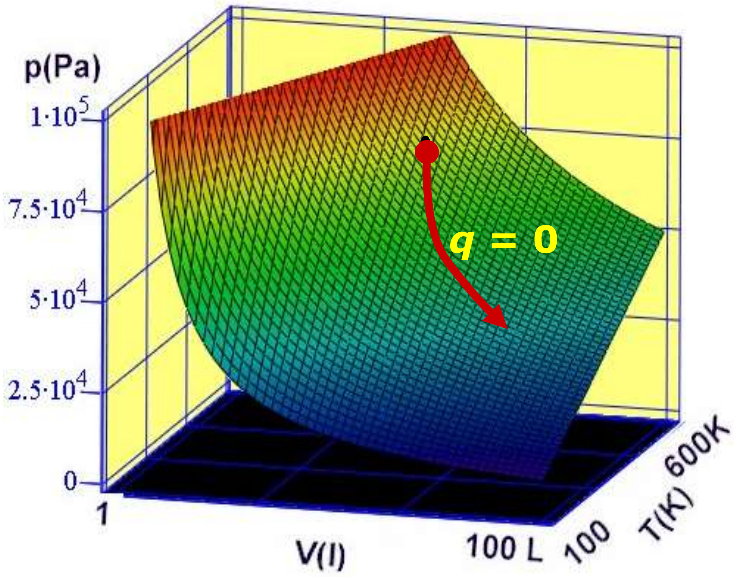
R = 8.2057 m³·atm/mol·K

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→ U
Non-interacting → Only gas phase!



Relation between internal energy of ideal gas and pressure-volume relation. Reversible adiabatic expansion means (here) no exchange of heat energy, d*q*=0, and no entropy change dS=0

$$dq = 0 \rightarrow dS = 0,\ dU = 0$$

Calculation for 1 mole ideal gas

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

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

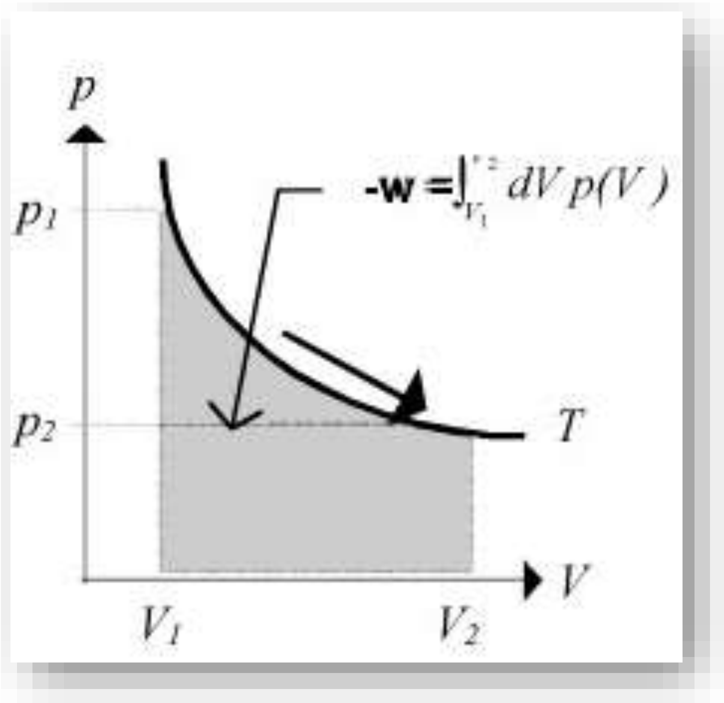
$$0 = C_V \cdot dT + p \cdot dV = C_V \cdot dT + \frac{R \cdot T}{V} \cdot dV$$

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

$$\gamma = \frac{c_p}{c_V}; \qquad \frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$$

$$\boxed{\begin{aligned} T \cdot V^{\gamma-1} &= const. \\ p \cdot V^{\gamma} &= const. \\ T^{\gamma} \cdot p^{1-\gamma} &= const. \end{aligned}}$$

Isothermal Expansion/Compression



w = - area under curve p(V)
Total work (1 →2):

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

$$w = -\int_1^2 p(V)\,dV = -R \cdot T \int_1^2 \frac{dV}{V} =$$

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

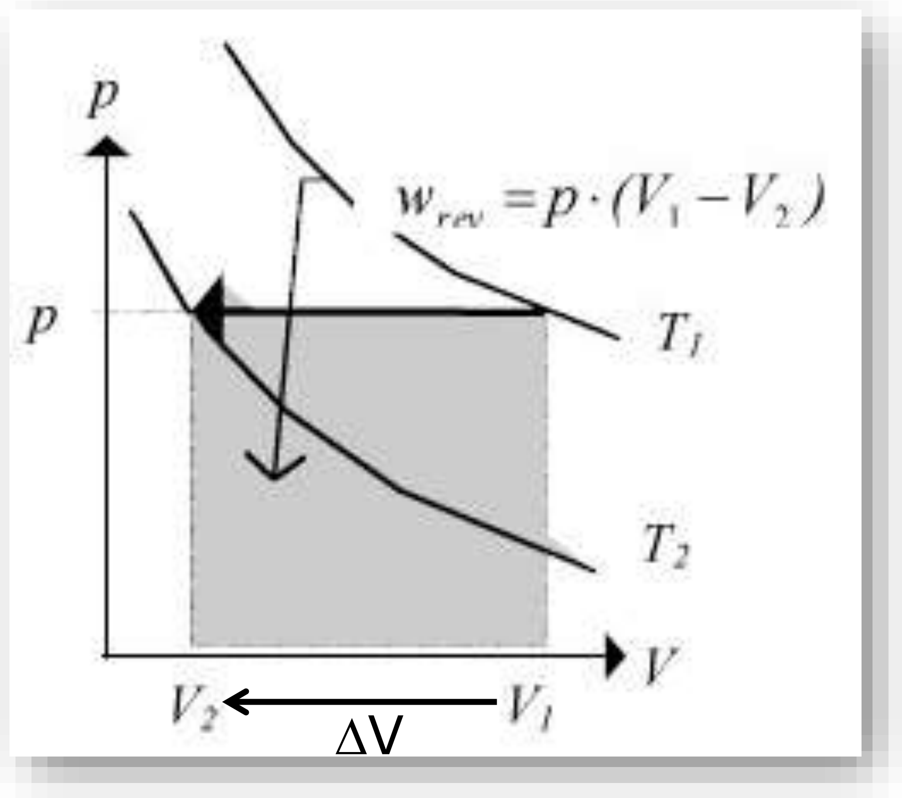
$$w < 0\ implies\ system\ does\ work$$
$$on\ surroundings$$

$$But\ \Delta U \propto \Delta T = 0 \ \rightarrow q > 0\ (absorbs\ heat)$$

$$\underline{1.\ LTD:}$$

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

Reversible Isobaric Compression



Internal energy change

Compress 1 mole at *p=const.*

Work done on system:

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

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

$\Delta T < 0$ *system cools by emitting*

$$q = C_p \cdot \Delta T = \frac{5}{2} R \cdot \frac{p \cdot \Delta V}{R} = -\frac{5}{2} w$$

Enthalpy change (*for* $p = const.$):

$$\Delta H = C_p \cdot \Delta T = C_p \cdot [T_2 - T_1] = q < 0$$

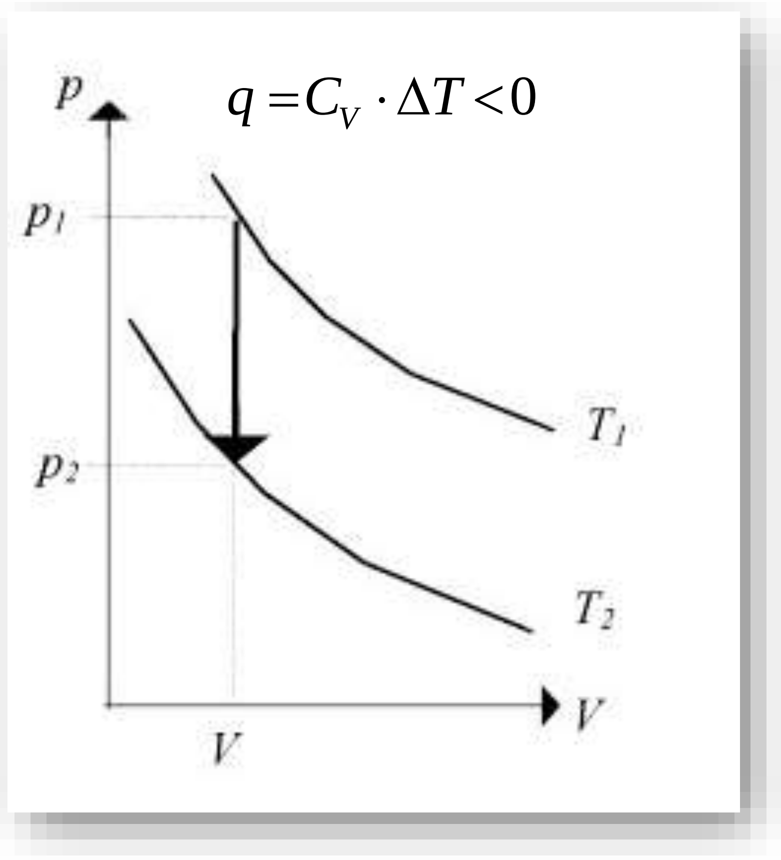
= emitted heat (internal energy)

$$\Delta U = q + w = (C_p - R) \cdot \Delta T$$

$$= C_V \cdot [T_2 - T_1] < 0$$

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

Reversible Decompression



Isochoric (V = const.) decompression
→ of 1 mole $w = -p\Delta V = 0$

$$\text{Work done on system } w = 0$$

$$\text{But } \Delta U < 0, \rightarrow \text{system emits heat}$$

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

$$1.\ \text{Law of Thermodynamics:}$$

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

$$\text{Enthalpy change}$$

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

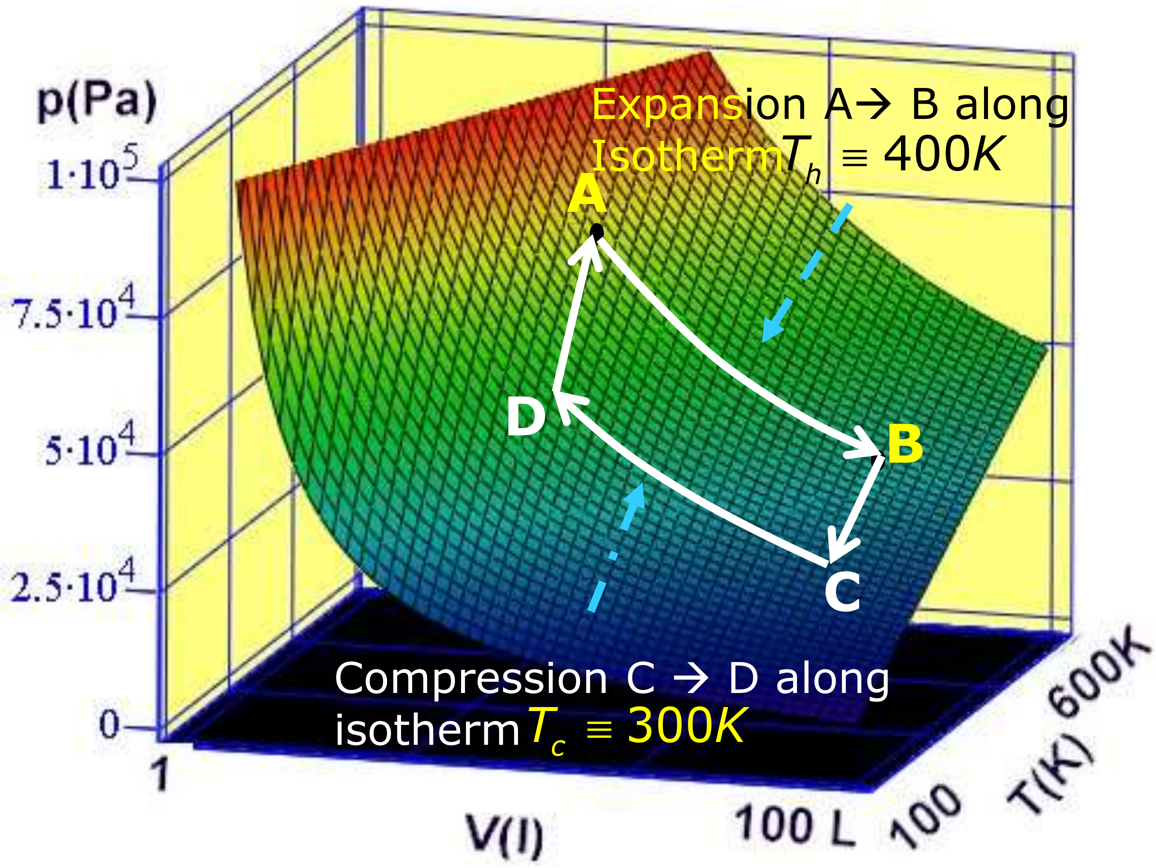
$$= C_p \cdot [T_2 - T_1] \quad (\text{always} = C_p \cdot \Delta T)$$

$$\text{NOTE}: \Delta H \neq q \ (\text{since } p \neq const)$$

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

Reversible Circular Processes on EoS Hyperplane

Ideal-Gas EOS $P \cdot V = R \cdot T$



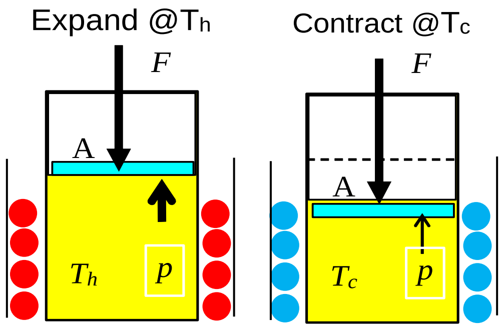
Expansion A→ B along Isotherm $T_h \equiv 400K$

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

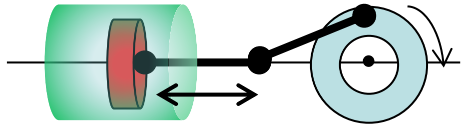
A circular process

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*

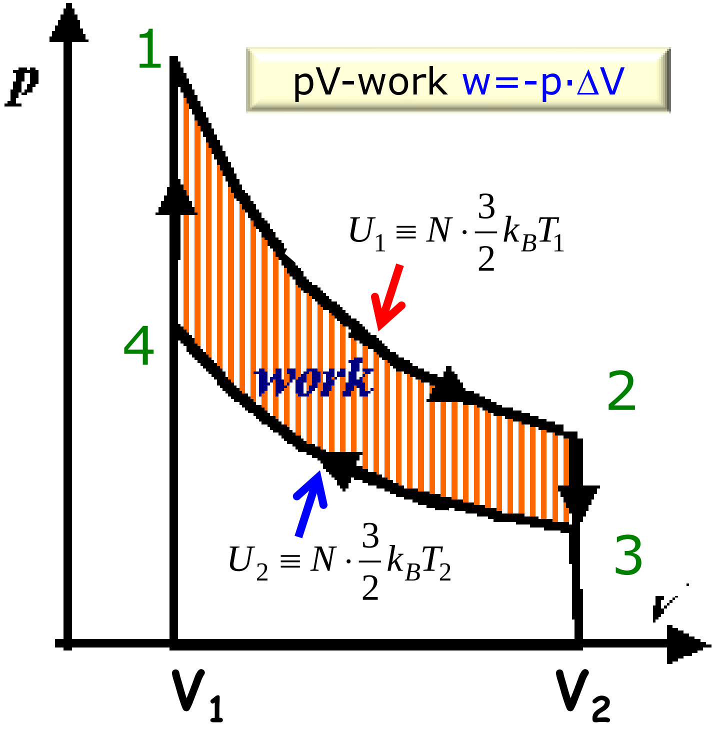
R = 0.0821 liter·atm/mol·K

R = 8.3145 J/mol·K

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

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



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 $w_2 = -q_2$; $\Delta U = 0$

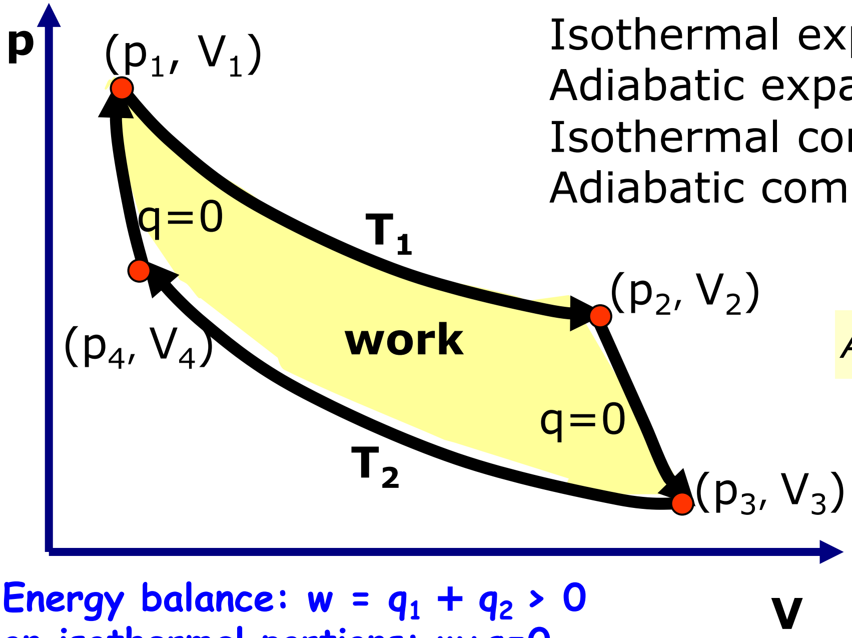
4-1 gas is heated $q > 0$; $\Delta U > 0$

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

Total heat absorbed: $\boldsymbol{q = q_1 + q_2 = -w > 0}$

Total work by engine : $\boldsymbol{w = w_1 + w_2 < 0}$

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

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

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

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

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

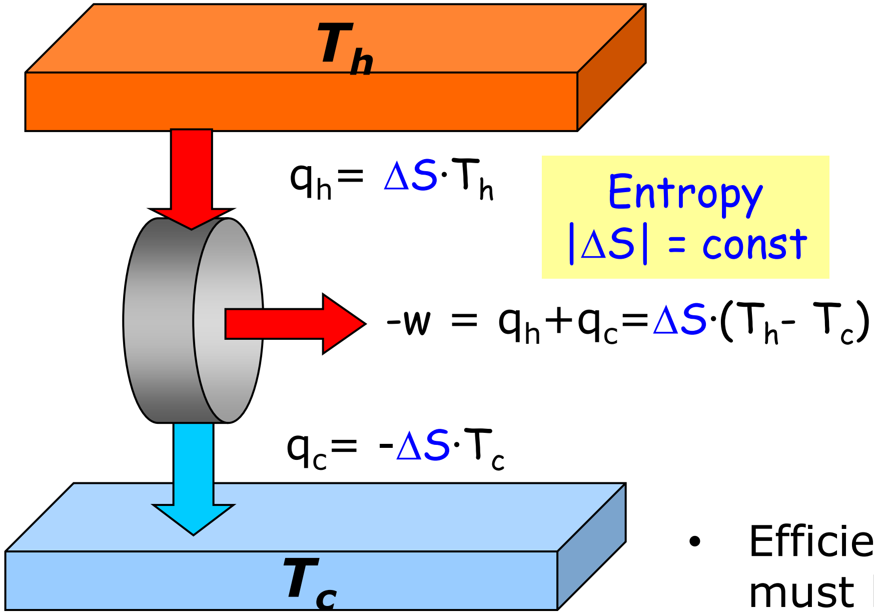
Entropy is conserved in reversible cyclic processes: $\Delta S_1 + \Delta S_2 = 0.$

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

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

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

Efficiency of Carnot Engines



Efficiency of an ideal Carnot engine

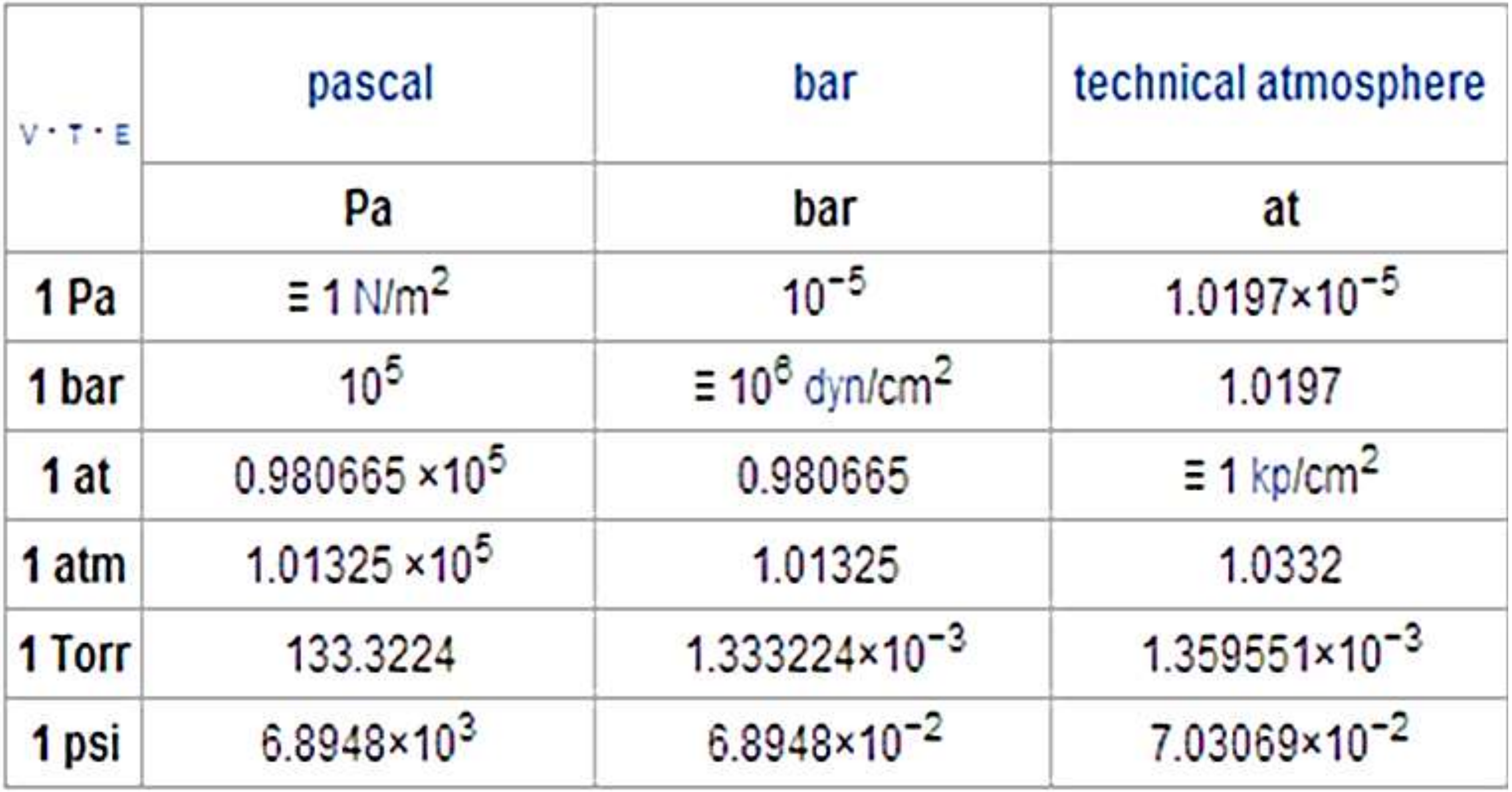
$$\varepsilon_C = \frac{-w}{q_h} = \frac{q_h + q_c}{q_h}$$

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

- 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	≡ 1 N/m^2	10^{-5}	1.0197×10^{-5}
1 bar	10^5	≡ 10^6 dyn/cm^2	1.0197
1 at	0.980665×10^5	0.980665	≡ 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}