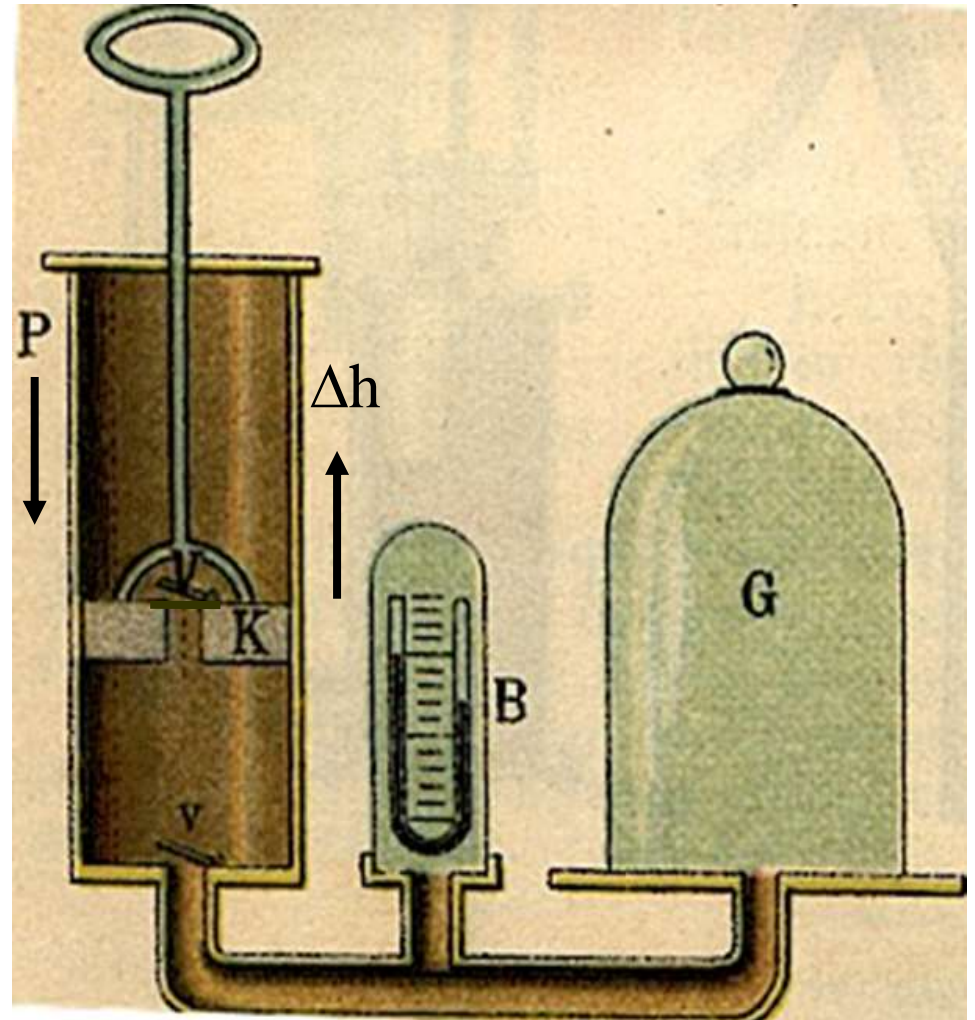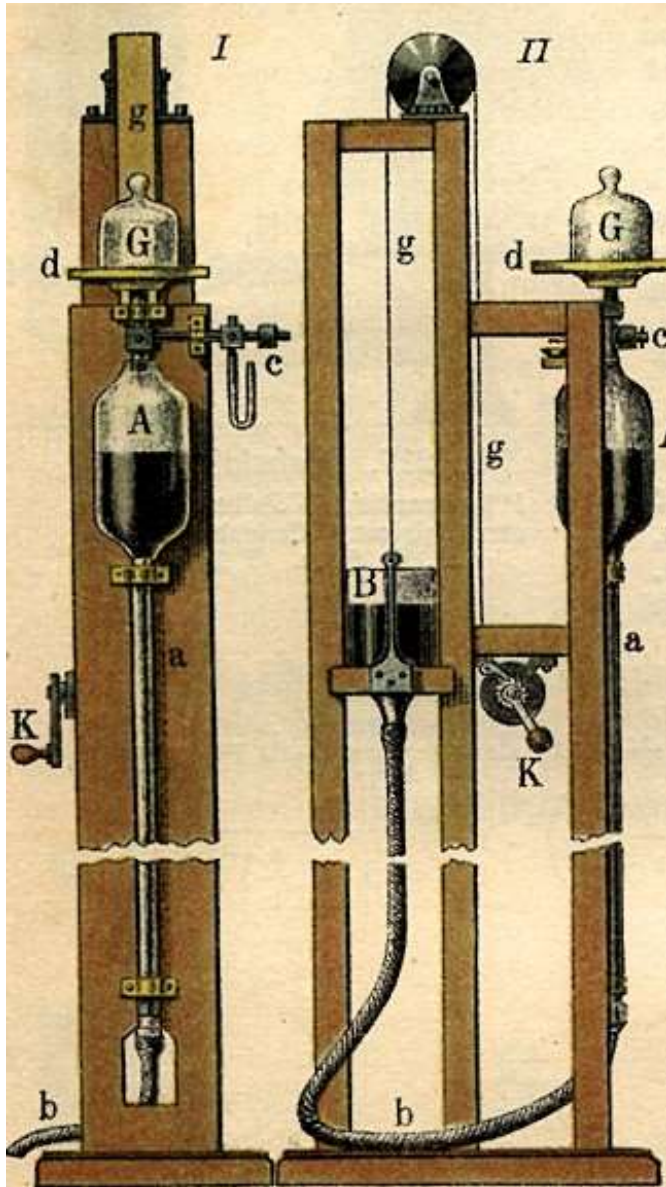# Thermodynamic Phenomenology & Applications

Thermodynamics: Phenomenology & Applications

- Work and other forms of energy

- Fundamental Laws of Thermodynamics

- Ideal-gas laws and simple processes

  Technological applications, cyclic engines

- Real gases equation of state

  Technological applications

- Phase equilibria, solutions

- Transport phenomena

Reading Assignments
Weeks 12&13
LN V-VI:

Kondepudi Ch. 3.5-3.7, 6 & 7
Additional Material

McQuarrie & Simon
Ch. 5 & 6

Evolution and Asymptotic State of Stochastic Systems

- Have considered the response of stochastic systems to external agitation. For example, multi-particle system (e.g., a gas) exposed to radiation, mechanical, or other work randomize initial disturbance by multiple interactions between system constituents (e.g., random collisions between gas particles).

- This dissipation process is directed towards increasing statistical entropy S (η-theorem). It takes some time to complete $S \rightarrow S_{max}$.

- After that, all particles in the system move randomly and share the total energy equally on average. $\rightarrow$ Fluctuations between equivalent microstates.

- This state is called "**Thermal Equilibrium**" (no memory of history)

  Extensive State Functions: N, V, internal energy U, entropy S, enthalpy H, free energies A, G. Intensive State Functions p, T.

- Predict probability distributions for <u>all</u> macroscopic observables: time-dependent means and variances.

Gas Laws: Ideal-Gas Equation of State EoS

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

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

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

$$Amontons'\ (Gay-Lussac's)\ Law \quad \boxed{P(T) = P(0) \cdot [1 + \alpha \cdot T_c] \propto T}$$

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

$\alpha \approx 3.66 \cdot 10^{-3}/^0 C \approx 1/273^0 C \rightarrow$ absolute temperature T
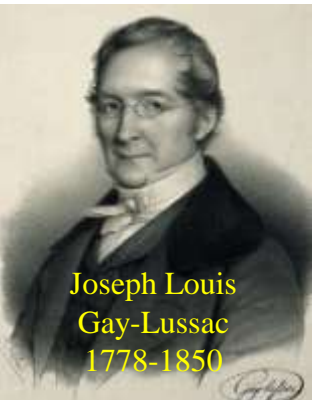
Compression
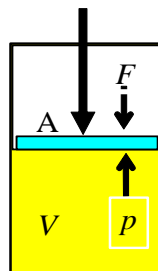
Robert Boyle: gas pressure ***p*** increases with external force $F = p \cdot A$, scales with number of particles *(N) or (n)* of gas moles

EoS of Ideal Gases $\boxed{P \cdot V = n \cdot R \cdot T = N \cdot k_B \cdot T}$

Equivalent $\boxed{P = \rho \cdot k_B \cdot T}$

$$Dalton's\ Law\ partial\ pressures\ \boxed{P = \sum_i P_i = \sum_i x_i \cdot P}$$

Amontons' Paper and Setup

DISCOURS SUR QUELQUES

propriétés de l'Air, & le moyen d'en connoître la température dans tous les climats de la Terre.

PAR M. AMONTONS.

Es expériences qui peuvent conduire à connoître la nature de l'air dans lequel nous vivons, font d'une conséquence affez confiderable pour mériter qu'on y faffe une particuliére attention. Celles que je fis il y a trois ans fur la dilatation de l'air par la chaleur de l'eau bouillante, me firent connoître que des maffes inégales d'air chargées de mêmes poids ou de poids égaux, augmentoient égale-ment la force de leur reffort par des degrés de chaleur égaux; & comme mon principal but dans ces expériences étoit de connoître de combien la chaleur de l'eau bouillante augmentoit le reffort de l'air au-deffus de ce qu'il en confer-ve dans l'eau que nous appellons froide, ces expériences me porterent pour lorsà croire que ce n'étoit que d'une quan-tité capable de foûtenir dix pouces en hauteur de mercure outre le poids de l'atmofphére : mais ayant depuis pouffé plus loin ces expériences, j'ai trouvé que le reffort de l'air augmenté par la chaleur de l'eau bouillante n'étoit pas fixé à ne foûtenir feulement que dix pouces de mercure plus que la charge de l'atmofphére ; mais qu'il en foûtenoit plus ou

1702. 28. Juin.
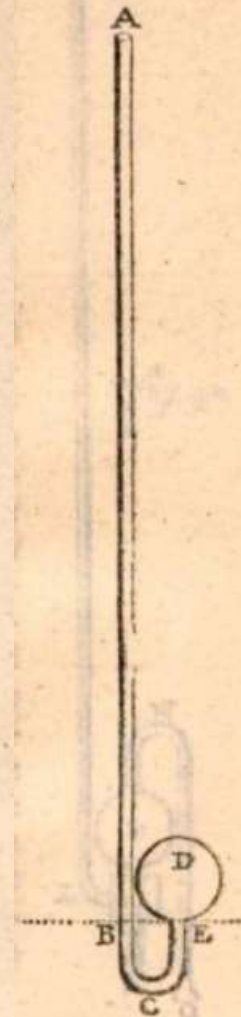
Mechanical Equivalent of Heat
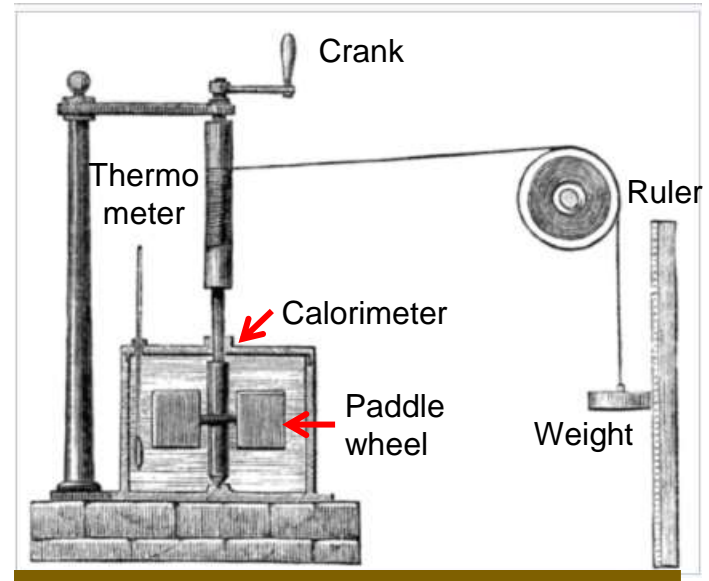

James Prescott Joule
1818-1889
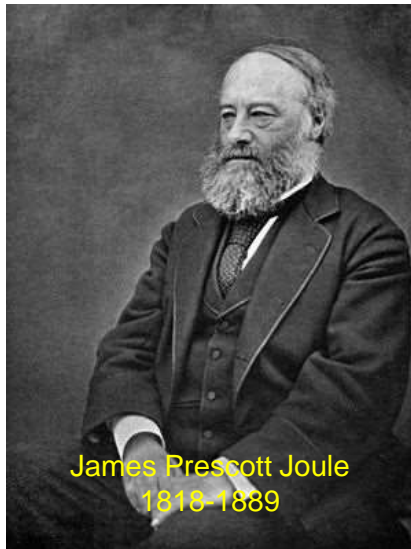
"An Experimental Enquiry Concerning the Source of the Heat which is Excited by Friction", (1798), Philosophical Transactions of the Royal Society p. 102
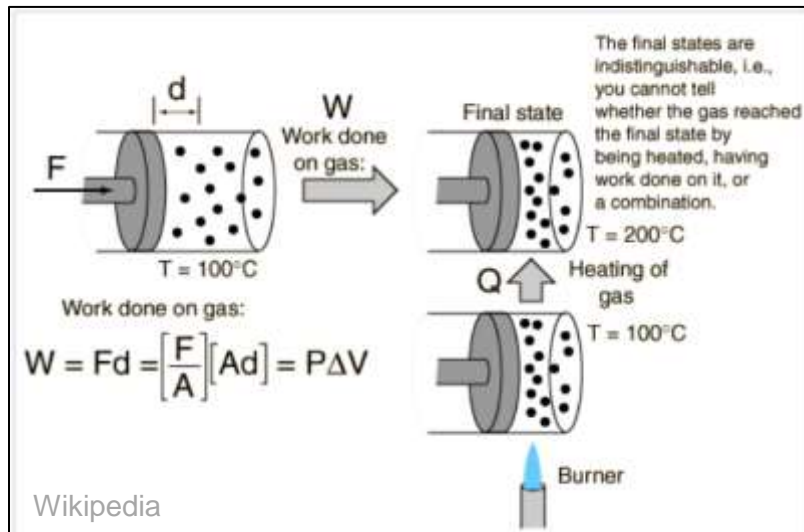
$$W \propto Q$$
$$\Rightarrow W = JQ$$
$$\Rightarrow J = \frac{W}{Q}$$

Joule's experiment

Crank

Thermo meter

Ruler

Calorimeter

Paddle wheel

Weight

The final states are indistinguishable, i.e., you cannot tell whether the gas reached the final state by being heated, having work done on it, or a combination.

Final state

$T = 200°C$

$T = 100°C$

Q — Heating of gas

$T = 100°C$

Work done on gas:
$$W = Fd = \left[\frac{F}{A}\right][Ad] = P\Delta V$$

Burner

Wikipedia

$$J = 4.186 \ kJ/kcal$$

$\approx$ specific heat of H_2O:
$C_V() \approx (4.17 - 4.22)$ J/(g·°C)

Ideal-Gas Equation of State EoS

Ideal-Gas Isotherms
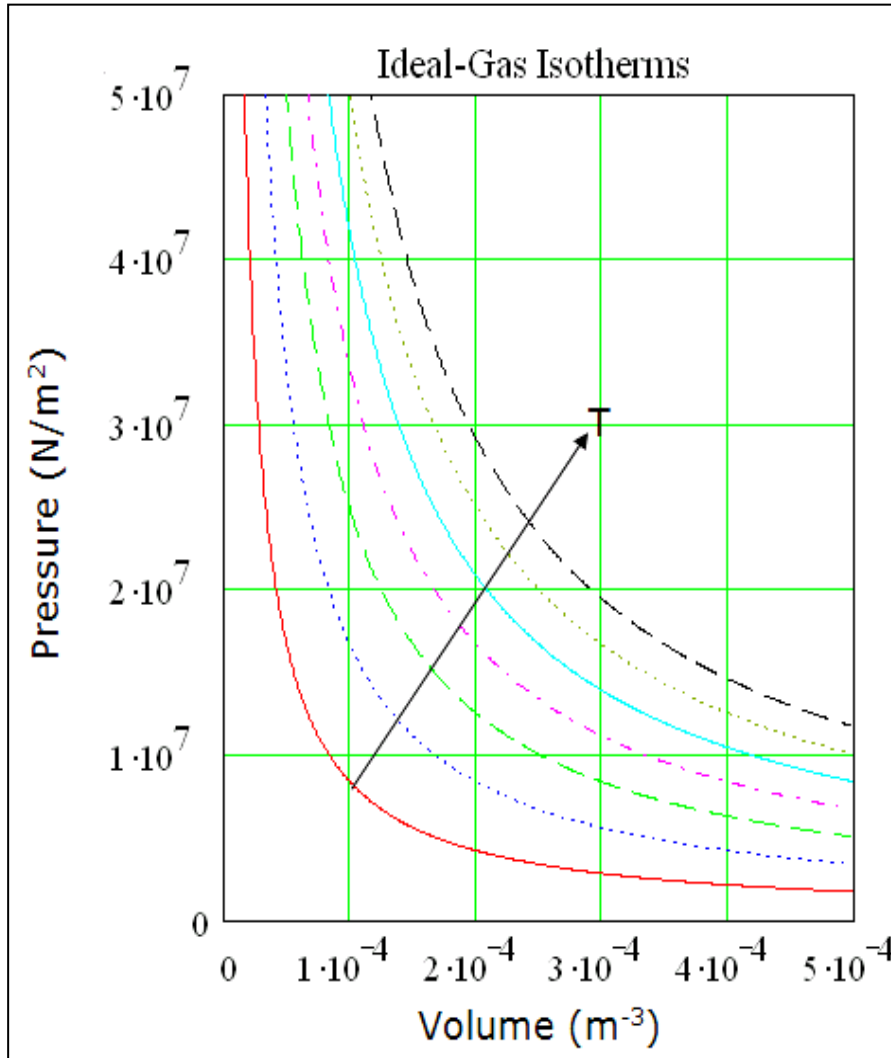
Complete description of macroscopic equilibrium state of any dilute gas:

Ideal gases have only one phase (*g*)

State Functions (variables)

Pressure *P*, volume *V*, temperature *T,*

Energy *U = <E>*, Entropy *S*
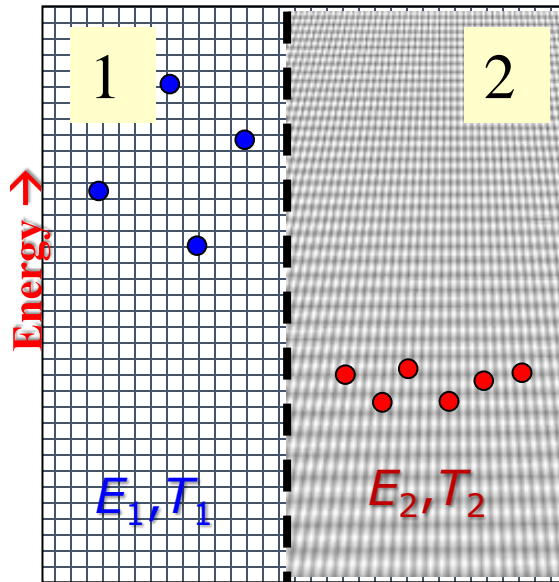
$$P \cdot V = n \cdot R \cdot T = N \cdot k_B \cdot T$$

Force $F = P \cdot A \rightarrow P \cdot V = energy\ content$

Entropy $S = n \cdot [R \cdot Ln\,V + C_V \cdot Ln\,T]$

Idealization: At *T=0* : *P* = 0, *V* = 0.
Idealization not viable at *T=0* high
high matter density → particles interact

Gas Constant   R = 8.31451 J/(K·mole)
Boltzmann Constant k_B = 1.38.10⁻²³ J/K

0. LTD: Systems in Thermal Contact Equilibrate

Disequilibrium: Systems, *1* and *2*, $T_1 \neq T_2$
individual particle numbers and energies,

$$N_1 + N_2 = N, \quad E_1 + E_2 = E = const.$$

\# of states: $\Omega_1(E_1)$ and $\Omega_2(E_2)$, **initial** (E_1, E_2)

Isolated combined system ***CS = 1+2*** :
$E_1 + E_2 = E = const$, but E_1/E_2 can vary through
heat *(q)* exchange $1 \leftrightarrow 2$ (no particles).

1 **Energy →** E_1, T_1

2 E_2, T_2

Observation: Systems in contact exchange energies until $T_1 = T_2$
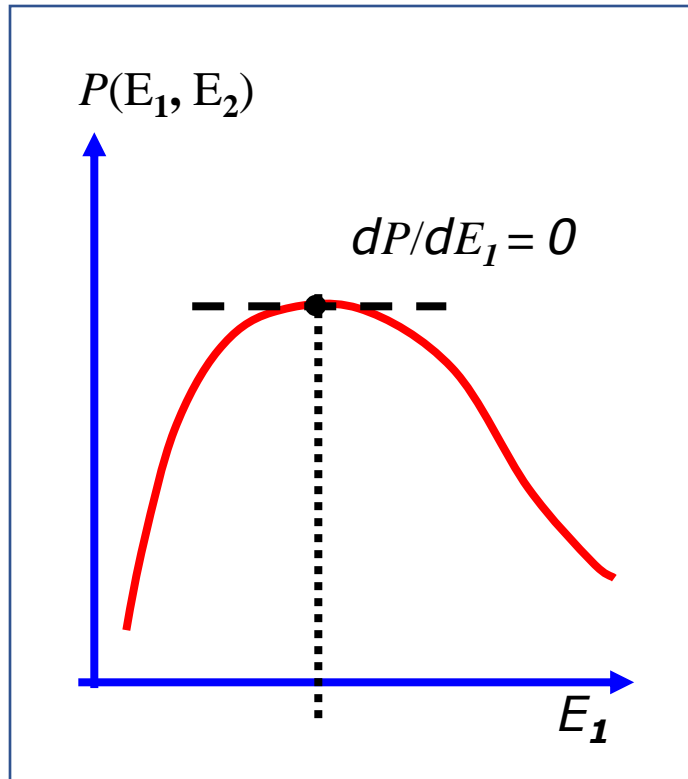
WHY? How likely is any E_1/E_2, how does it evolve in time?

→ *Heuristic argument* ≈ postulate, specific for *q* exchange $1 \leftrightarrow 2$:

Maximize $\quad P(E_1, E_2) \propto \Omega_{CS}(E_1, E_2) = \Omega_1(E_1) \cdot \Omega_2(E_2) = \Omega_1(E_1) \cdot \Omega_2(E - E_1)$

Maximizing Opportunities (# of accessible states)

$P(E_1, E_2)$

$dP/dE_1 = 0$

E_1

Heuristic argument: Maximize $P(E_1, E_2)$

$P(E_1, E_2) \propto \Omega_{CS}(E_1, E_2) = \Omega_1(E_1) \cdot \Omega_2(E - E_1)$

Conservation of total energy $E = E_1 + E_2 = const$

Heat energy (q) transfer $\rightarrow$ probability change,

constraint $\Delta E_1 = -\Delta E_2 < 0$

Product rule :

$$\frac{dP}{dE_1} \propto \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) + \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_1}$$

$$= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2}$$

$$Maximum\, P: \boxed{\frac{dP}{dE_1} = 0} \rightarrow \quad \frac{1}{\Omega_1}\frac{d\Omega_1(E_1)}{dE_1} = \frac{1}{\Omega_2}\frac{d\Omega_2(E_2)}{dE_2} \neq 0$$

We already know: If configurations are equally likely $\rightarrow$ P maximizes entropy (η)

Entropy and Energy at Equilibrium

Systems $(1, 2..., N)$ *in mutual contact* $\rightarrow$ *eventual stationary state* $=$ *maximum probability*

all acquire *same* (*but lower*) *temperature T when*

$$\left(\frac{1}{\Omega} \frac{d\Omega(E)}{dE} \right)_1 = \left(\frac{1}{\Omega} \frac{d\Omega(E)}{dE} \right)_2 .... = \left(\frac{1}{\Omega} \frac{d\Omega(E)}{dE} \right)_N \quad \Rightarrow \quad \frac{d\Omega(E)}{\Omega dE} = \frac{d\ln[\Omega(E)]}{dE} = const.(E)$$

Const(E) dim=1/energy: *Independent of material, size, shape, amount*.
$\rightarrow$ Depends on energy supplied to one of the systems.
But is not extensive!

Suspect Const. $\sim$ temperature **T** = intensive observable that depends on energy, since $P \cdot V = N \cdot k_B \cdot T$

Construct **intensive** energy-related variable $\quad \frac{d\ln[\Omega(E)]}{dE} \propto \frac{d[S(\langle E \rangle)]}{d\langle E \rangle} \propto \frac{1}{T}$

Define $S = k_B \cdot Ln\,\Omega \rightarrow \frac{\partial S}{\partial E} = k_B \cdot \beta$

$$S(\langle E \rangle) \sim S_0 + \frac{\langle E \rangle}{T}$$

Boltzmann Constant

integration constant

Simplest form compatible: Entropy ("intrinsic") *S extensive*, with $S_0=0$

Deduced from Observation: Entropy at Equilibrium

Ludwig Boltzmann
1844-1906

System with $\Omega = \#\,intrinsic\,states,$ *initially in g.s.* $T_{sys}, E \approx 0;\, S \approx 0$

brought in contact with "Heat Bath" $@\,T_{heat\,bath}$ *spontaneously*

acquires heat energy $\Delta\langle E\rangle = \Delta q \rightarrow$ *stationary state*

Thermal Equilibrium :

Maximum spread of $\Delta\langle E\rangle$ *over* Ω, *system* $\rightarrow T_{sys} \approx T_{heat\,bath}$

Heat absorption /
emission by system $@T_{sys}$ $\quad : \Delta\langle E\rangle = \Delta q \rightarrow$ $\boxed{\Delta S = \dfrac{\Delta q}{T_{sys}}}$ $\Rightarrow$ $\boxed{\begin{array}{l} S(E) = S_{max}(E) \\[8pt] S(\langle E\rangle) = \dfrac{\langle E\rangle}{T_{sys}} \geq 0 \end{array}}$

Sign ΔS = sign Δq

In spontaneous processes, entropy (always) increases: $\Delta S > 0$

$$\boxed{S(E) = k_B \cdot Ln\,\Omega(E) \geq 0} \qquad \boxed{\Omega(E) = e^{S(E)/k_B} \geq 1}$$

$$k_B = 1.380649 \times 10^{-23}\,J/K = 1.380649 \times 10^{-16}\,erg/K$$

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  Carnot process

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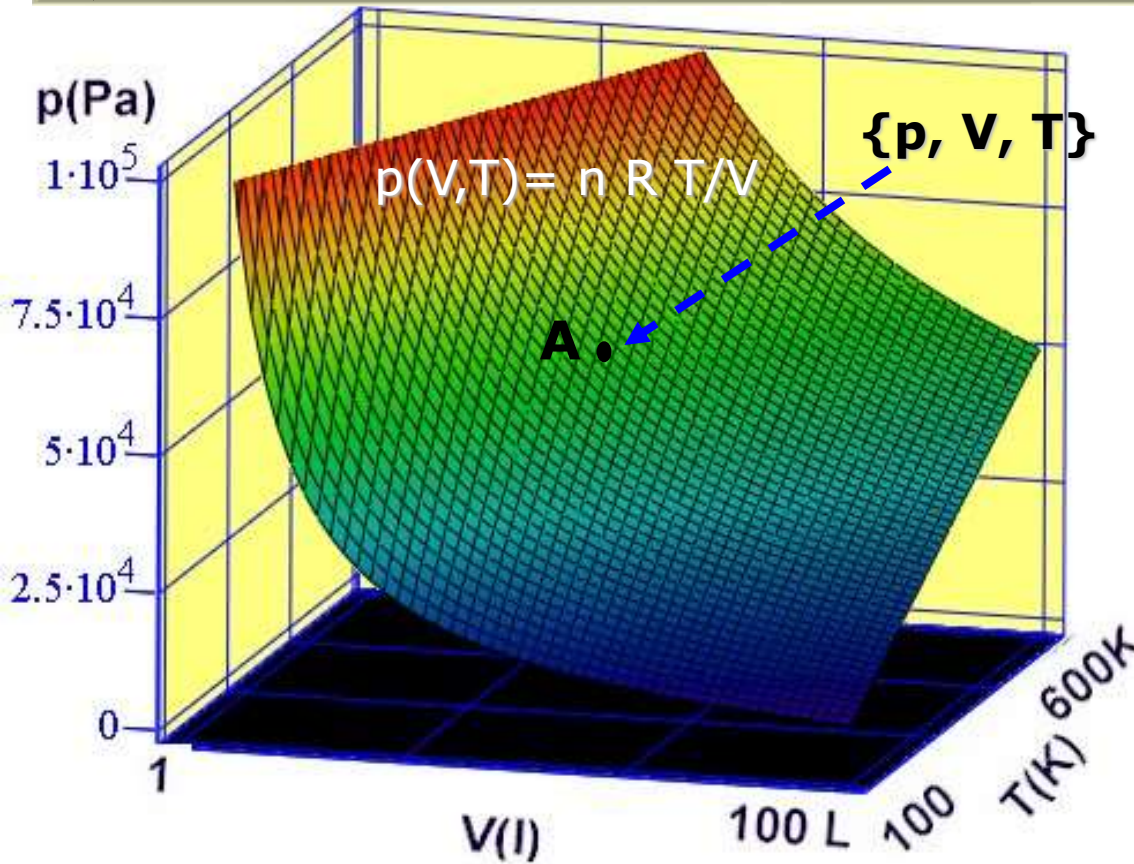Additional Material

McQuarrie & Simon
Ch. 5 & 6

The Ideal-Gas Equation of State

$p \cdot V = n \cdot R \cdot T$; n=# moles; equivalent: $p \cdot V = N \cdot k_B \cdot T$ (N=# particles)

➡ Internal energy $U/N \equiv \langle E/N \rangle = (3/2) k_B \cdot T$ $T \longleftrightarrow U$ Only gas phase!

$p(V,T) = n R T/V$

{p, V, T}

A.

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·

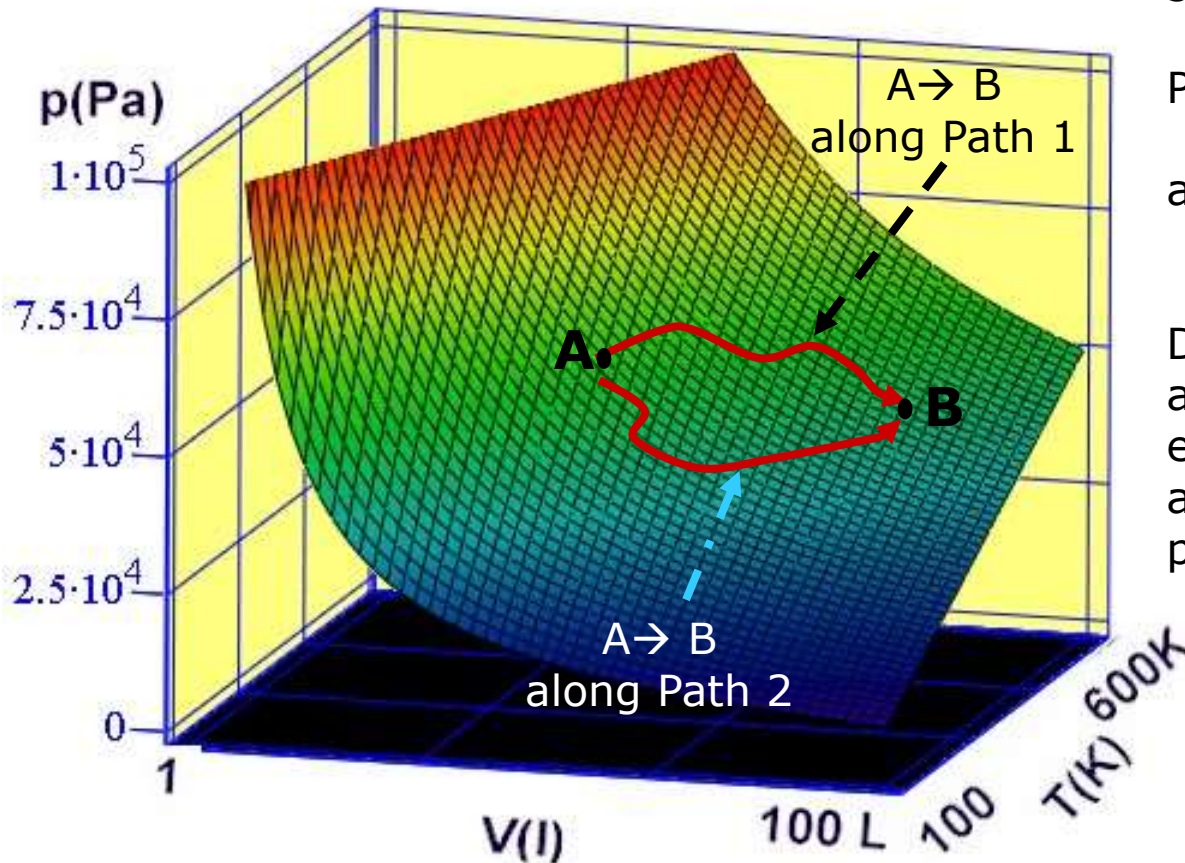**Boltzmann Constant k_B**

k_B = 1.381·10^{-23} J/K

$$dU = T \cdot dS + w_{pV} = T \cdot dS - p \cdot dV$$

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

Ideal gas

Transitions Between States

Ideal-Gas EOS

p(Pa)

$1 \cdot 10^5$

$7.5 \cdot 10^4$

$5 \cdot 10^4$

$2.5 \cdot 10^4$

0

1

V(l)

100 L

100

600K

T(K)

A

B

A→ B along Path 1

A→ B along Path 2

A, B: Two states of the same gas.

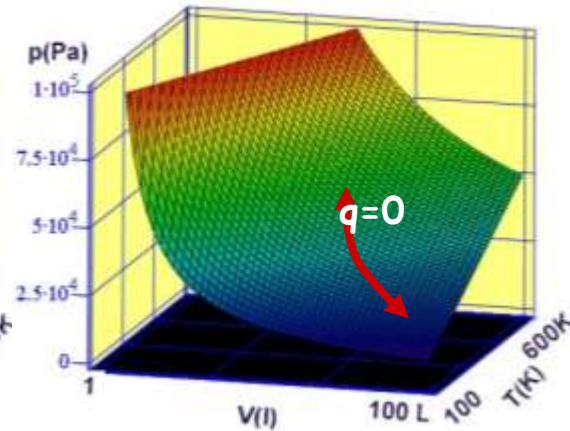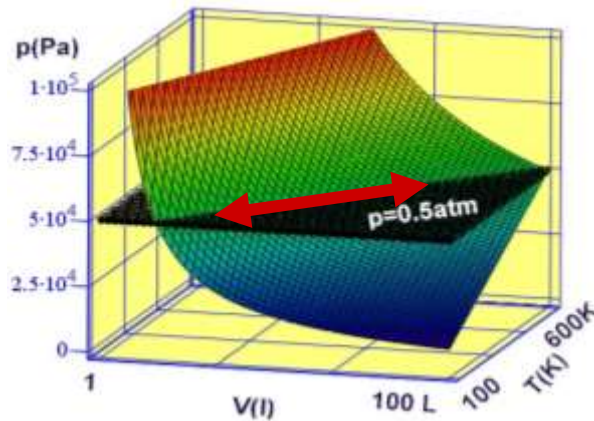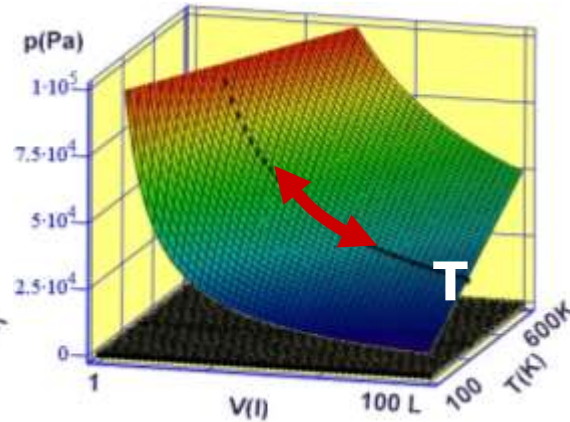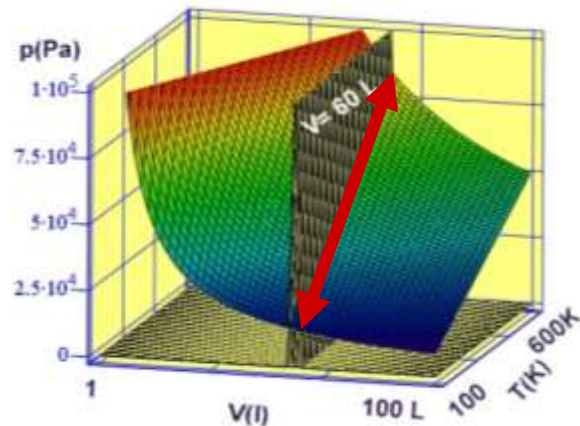Processes $A \xrightarrow{\;\;1\;\;} B$

and $A \xrightarrow{\;\;2\;\;} B$

Differ by different types and relative amounts of energy transfer via absorption of heat and performance of work.

State functions *p, V, T, S,...* describe the system states but not the processes connecting them.

Reversible Processes

Of interest for cyclic machines.

Slow, equilibrium processes A → B, subject to equilibrium boundary conditions of:

1. **Δp = 0   (isobaric)**

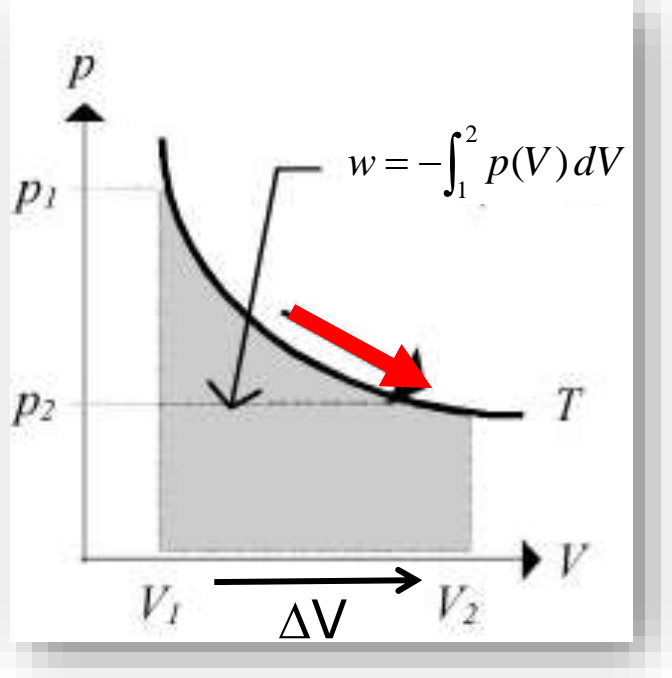2. **ΔV = 0   (isochoric)**

3. **ΔT = 0 (isothermal)**

4. **q = 0   (adiabatic)**

follow well-defined, constrained routes in the {p, V, T} hyper-plane of states. Can, in principle, be inverted →reversible processes.

Reversibility is not guaranteed for all processes involving an ideal gas. Need to maintain equilibrium throughout process.

Reversible Isothermal Expansion/Compression

Slow, reversible expansion under retention of equilibrium, $S = S_{max}(T)$

Intersection of {p,V,T} hyper-plane with plane T=const.

$$w = -\int_1^2 p(V)\,dV$$

ΔV

w = - area under curve p(V)
Total work ($V_1 \rightarrow V_2$):

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

$$w = -\int_1^2 p(V)\,dV = -R \cdot T \int_1^2 \frac{dV}{V} =$$
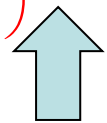
$$= R \cdot T \cdot \ln\left(\frac{V_1}{V_2}\right) < 0$$

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

$\quad on\ surroundings$

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

$1.\ Law\ of\ Thermodynamics:$

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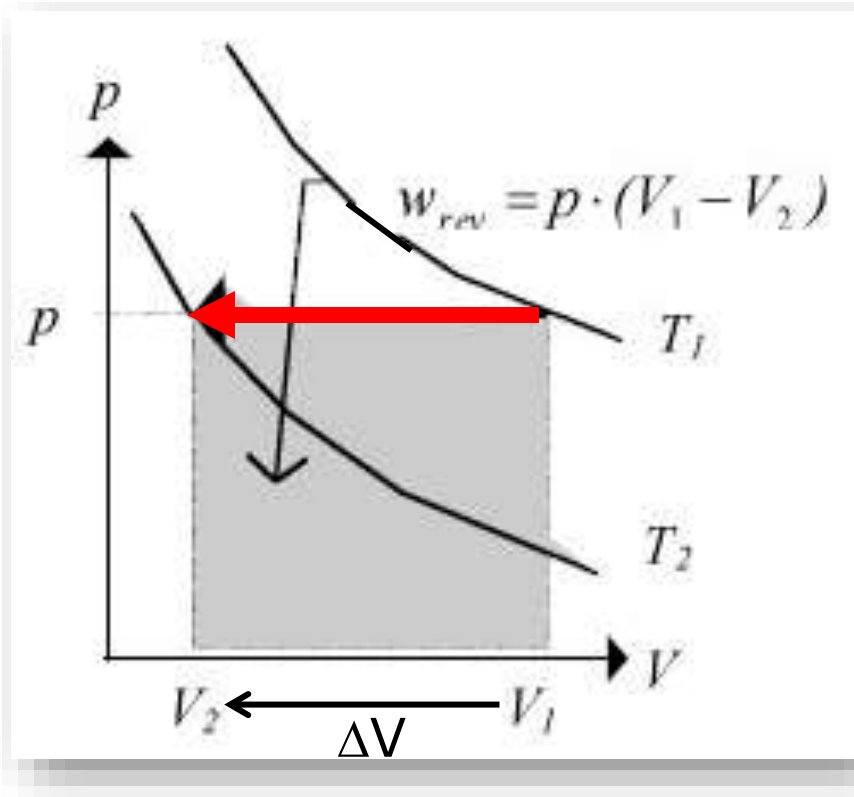
Reversible Isobaric Compression

Slow, reversible compression under retention of equilibrium, $S=S_{max}(T)$

Work done on system:

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

$$= -p\cdot\Delta V = -R\cdot\Delta T > 0 \quad Shaded\ Area$$

⌐ EOS ⌐

$\Delta T < 0$: system must cool by emitting

$$q = C_p\cdot\Delta T = \frac{5}{2}R\cdot\left(\frac{p\cdot\Delta V}{R}\right) = -\frac{5}{2}w < 0$$

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

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

= emitted heat (internal energy)

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

Internal energy change ➡ $\boxed{\Delta U = C_V\cdot[T_2 - T_1] < 0}$

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 of its cylinder.

The figure shows a p-V diagram with two isotherms T_1 and T_2, a shaded area representing $w_{rev} = p\cdot(V_1 - V_2)$, with volumes V_2 and V_1 marked along the horizontal axis and ΔV between them.

Reversible Decompression

Slow, reversible expansion under retention of equilibrium, $S = S_{max}(\boldsymbol{T})$

$$q = C_V \cdot \Delta T < 0$$
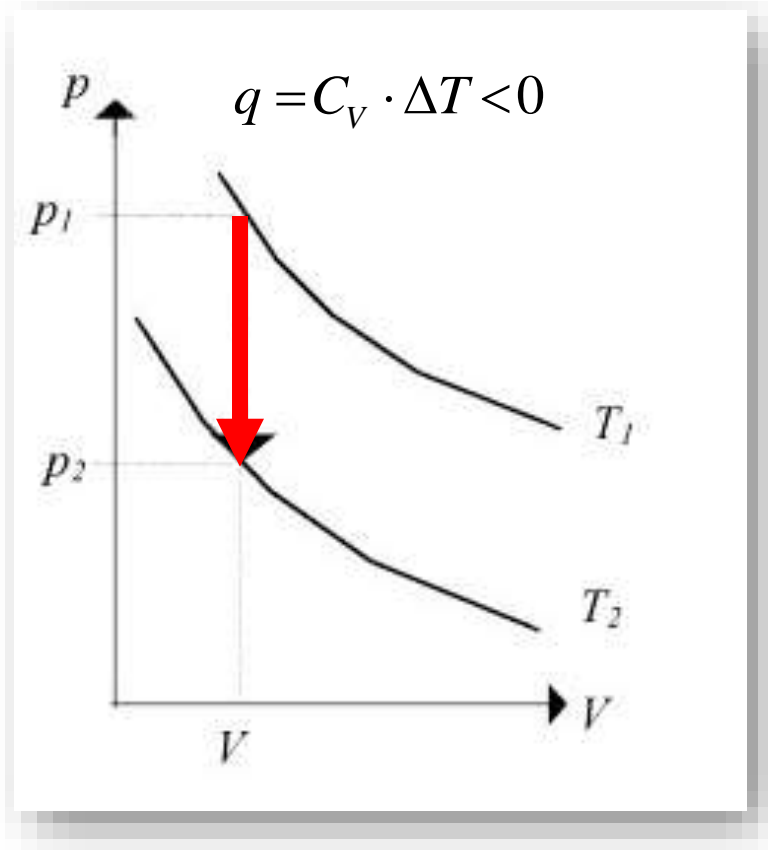
Work done on system $w = 0$

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

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

1. *Law of Thermodynamics:*

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

Enthalpy change

$$\Delta H = \Delta U + \Delta(pV) = (C_V + R) \cdot \Delta T$$
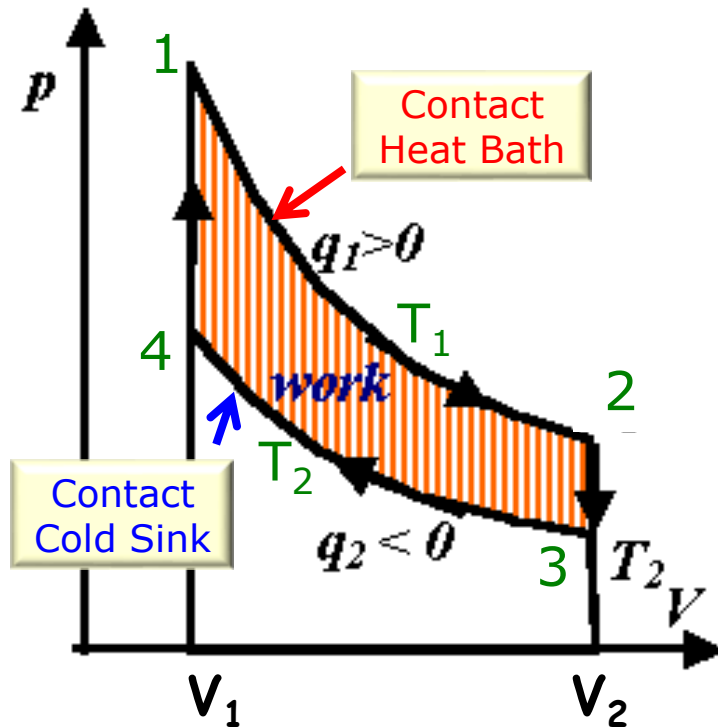
$$= C_p \cdot [T_2 - T_1] \quad \left(always \; \Delta H = C_p \cdot \Delta T \right)$$

BUT $\boxed{\Delta H \neq q \; (since \; p \neq const)}$

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

Expansion-Compression Cycles

Observation: IG systems absorbing external (random) heat can produce mechanical work on surroundings (=engine). Continuous operation requires cyclic process (in p-V-T space).

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.,

Energy balance:

1) gas does work	$w_1 = - q_1$;	$\Delta U = 0$
2) gas emits heat	$q < 0$;	$\Delta U < 0$
3) gas receives work	$w_2 = - q_2$;	$\Delta U = 0$
4) gas absorbs heat	$q > 0$;	$\Delta U > 0$

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

Total work done: $w = w_1 + w_2 < 0$
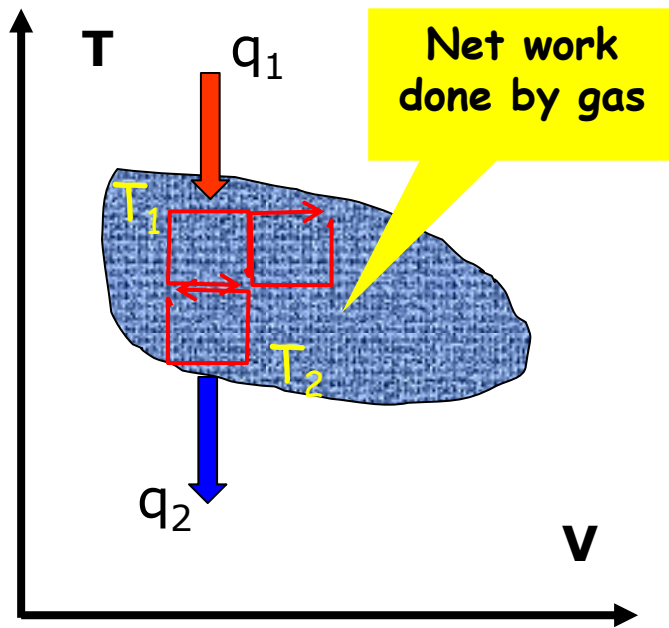
Total heat absorbed: $q = q_1 + q_2 = -w > 0$

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

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

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

Thermal Engines: Principle of Operation

T q_1

Net work done by gas

T_1

T_2

q_2

V

Horizontal paths traveled in both directions do not contribute net work → Area within closed p-V paths = total work done in cyclic process.
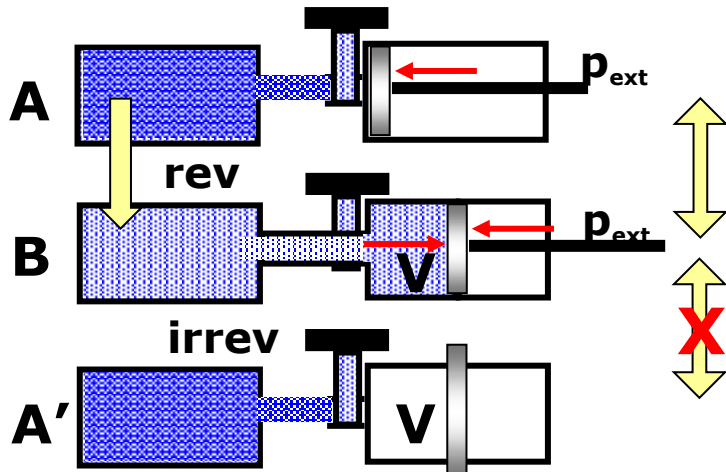
Make an arbitrary cyclic process out of elementary isothermal and isochoric processes →

Heat energy q_1 is absorbed at a high temperature(s) T_1, and partially dumped, $|q_2| < |q_1|$, at a lower temperature(s) T_2.

The difference $(q_1 + q_2) = q_1 - |q_2|$ is converted into useful work $w < 0$ done on surroundings by the gas.

Random heat energy is converted into orderly collective energy (work, pushing a piston, turning a wheel) !!!!!!! → Practical use

Work/Heat in Reversible vs. Irreversible Processes

A

rev

B

p_{ext}

p_{ext}

V

irrev

A′

V

Opening valve: Expansion →**B**, **B′**

p_{gas}

A

rev expansion
q=0

irrev expansion

max work capacity ∫pdv

p_{ext}

B   **B′**

A′

V

System interacts with environment, is not isolated (ΔT=0).

In process A → B, carried out so that system is always at equilibrium (e.g, p_{ext} dV= p_{gas}dV+q), system produces maximum work.
(balance by *including the –sign, sign convention!*):

$$\mathbf{w_{rev} < w_{irrev}} \rightarrow |w_{rev}| > |w_{irrev}|$$

Where did the difference Δ**w** go ? Nowhere!
Also less/no heat absorbed on irreversible path.

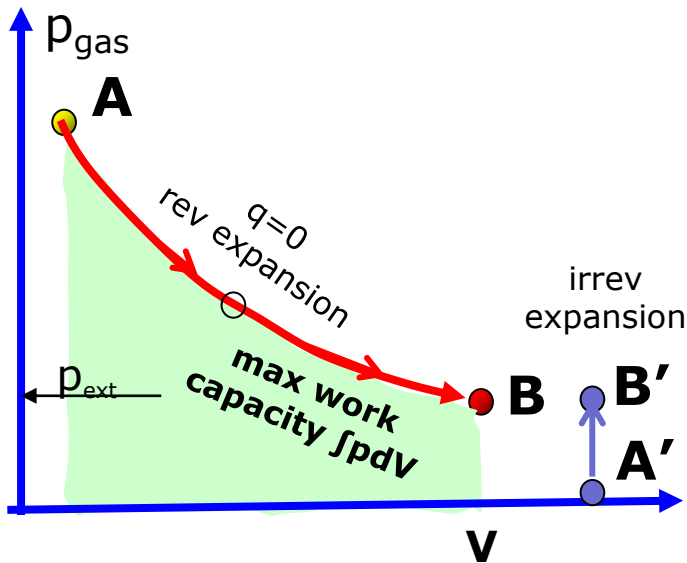1. Law TD, and since ***U*** is a state function,

$$\text{If } \Delta U_{A\rightarrow B} = \Delta U_{A'\rightarrow B} \rightarrow (q+w)_{rev} = (q+w)_{irrev}$$

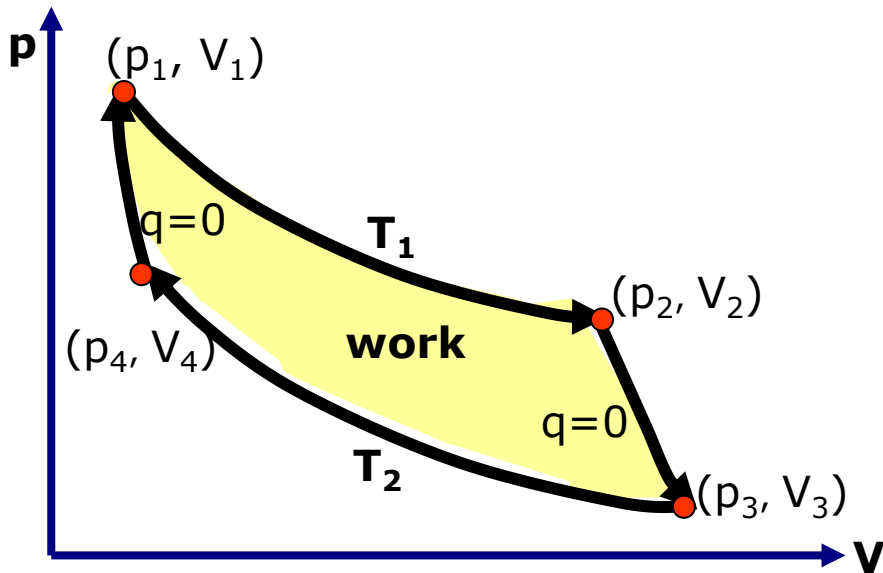$$\rightarrow \quad w_{rev} < w_{irrev} \quad \leftrightarrow \quad q_{rev} > q_{irrev}$$

w_{rev} is largest amount deliverable (negative) reversibly → q_{rev} is largest amount of heat system can absorb reversibly and convert into work.

Irreversible, spontaneous processes:
Less efficient conversion of absorbed heat into useful work.

Carnot Cycles

(p_1, V_1)

q=0

T_1

(p_4, V_4)

work

(p_2, V_2)

q=0

T_2

(p_3, V_3)

p

V

Adiabatic $(q = 0)$ *EoS*

$T \cdot V^{\gamma-1} = const$; $\quad \gamma = c_p / c_V$

Similar to previous examples, but adiabatic expansion $T_1 \rightarrow T_2$ adiabatic compression $T_2 \rightarrow T_1$

Adiabatic pdV works cancel because
$V_4/V_1 = V_3/V_2 \rightarrow V_4/V_3 = V_1/V_2$

Energy balance: w = q$_1$ + q$_2$ > 0 on isothermal portions:

$$q_1 = -w_1 = \int_{V_1}^{V_2} \underset{\propto 1/V}{p} \, dV = R \cdot T_1 \cdot \ln\left(\frac{V_2}{V_1}\right) > 0$$

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

$$\rightarrow w = w_1 - w_2 < 0 \rightarrow system \ does \ net \ work$$

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

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

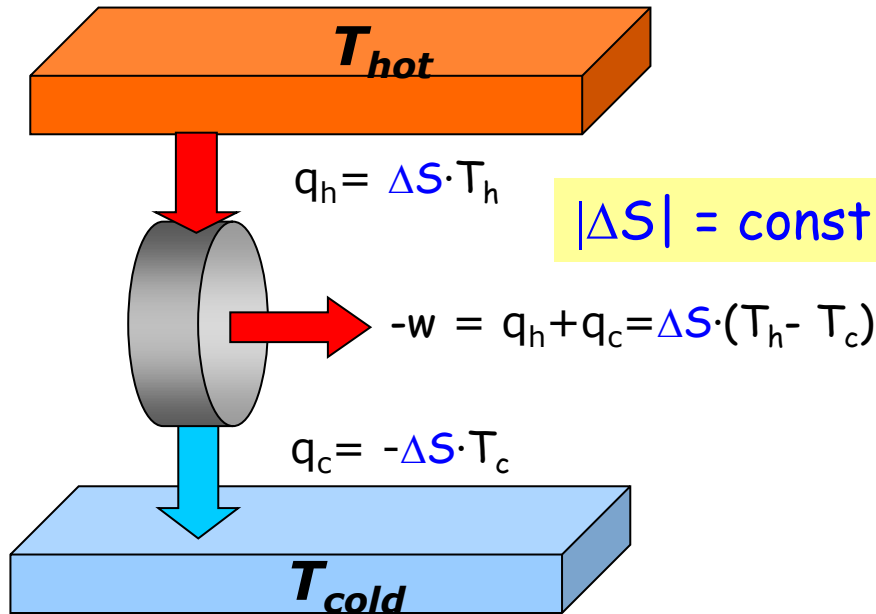$\rightarrow S = state \ function \ (descriptor)$

$q_1 = T_1 \cdot \Delta S_1 \qquad q_2 = T_2 \cdot \Delta S_2$

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.: $\Delta S > 0$.

Efficiency of Carnot Engines

T_{hot}

$q_h = \Delta S \cdot T_h$

$|\Delta S| = const$

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

$q_c = -\Delta S \cdot T_c$

T_{cold}

Theoretical Carnot efficiency

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

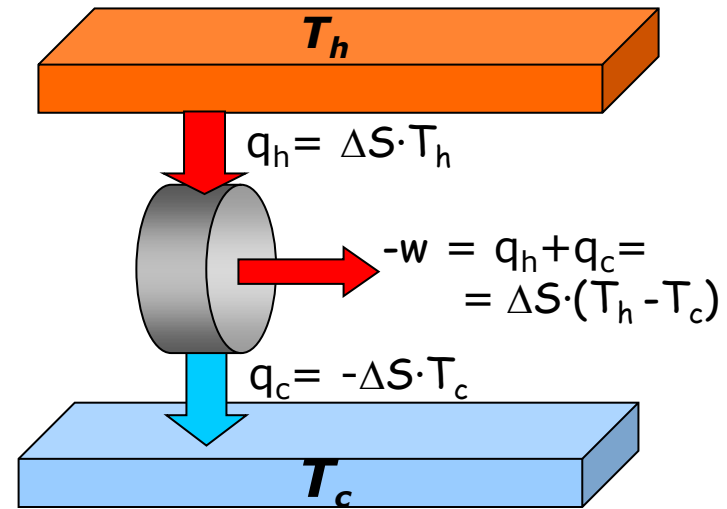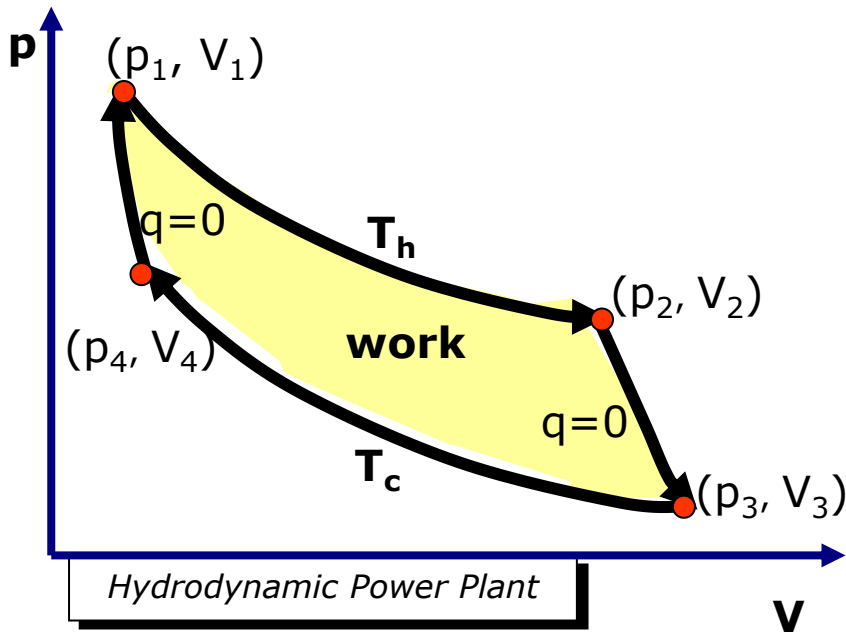$$\varepsilon_C = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \xrightarrow[T_h \to \infty]{} 1$$

Typical Carnot cycle efficiency achieved: $\varepsilon_C \approx (30\text{-}40)\%$

In practice, T_h of heat bath depends on fuel heating value (max temperature T_{ad}). Transfer from fuel to heat reservoir: $\quad \varepsilon_F = (T_{ad} - T_h)/(T_{ad} - T_c)$

→ Effective Carnot efficiency: $\quad \varepsilon = \varepsilon_C \cdot \varepsilon_F = \left(1 - \frac{T_c}{T_h}\right) \cdot \left(\frac{T_{ad} - T_h}{T_{ad} - T_c}\right)$

Entropy Flow in Carnot Engines

p

(p_1, V_1)

$q=0$

T_h

(p_4, V_4)

work

(p_2, V_2)

$q=0$

T_c

(p_3, V_3)

Hydrodynamic Power Plant

V

T_h

$q_h = \Delta S \cdot T_h$

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

$q_c = -\Delta S \cdot T_c$

T_c

Entropy ΔS from the hot reservoir enters the engine with a heat energy of $\Delta S \cdot T_h$, **produces work** and leaves it again with a heat energy of $\Delta S \cdot T_c$, which is dumped into the cold sink.

$\Delta M \cdot g \cdot h_1$

Inlet

Reservoir

$\Delta M \cdot g \cdot h_2$

Turbine

Outlet
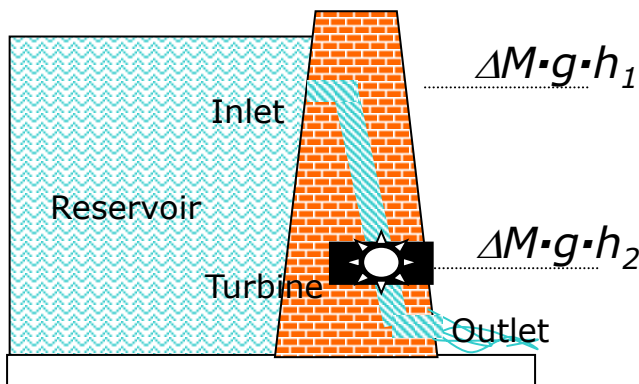
Analog: Stream of water ΔM from a reservoir carries energy $\Delta M \cdot g \cdot h_1$, enters a hydro-turbine, produces work, and leaves with an energy $\Delta M \cdot g \cdot h_2$, which is dumped into the river.

Mass flow $j_M \propto dM/dt$. Entropy flow $j_S \propto dS/dt$

Steady-Flow Processes

1. Law of Thermodynamics
(Conservation of total energy in isolated system):

$$E = U + \frac{1}{2} M v^2 + V_{pot}$$

M = mass, v = velocity, V_{pot} = potential energy (often ≈0)
Mass density $\rho = \rho_m$ (kg/m³), homogeneous
Internal energy density u (J/m³)
Enthalpy density $h = u + p$

Internal energy $\quad dU_i = u_i \cdot (A_i \cdot dx_i) \qquad\qquad dV_i = A_i \cdot dx_i$

Kinetic energy $\quad dK_i = (1/2)\, \rho_i \cdot v_i^2 \cdot (A_i \cdot dx_i)$

Mechanical work $\quad dW_i = p_i \cdot (A_i \cdot dx_i)$

Carried by mass flow through system

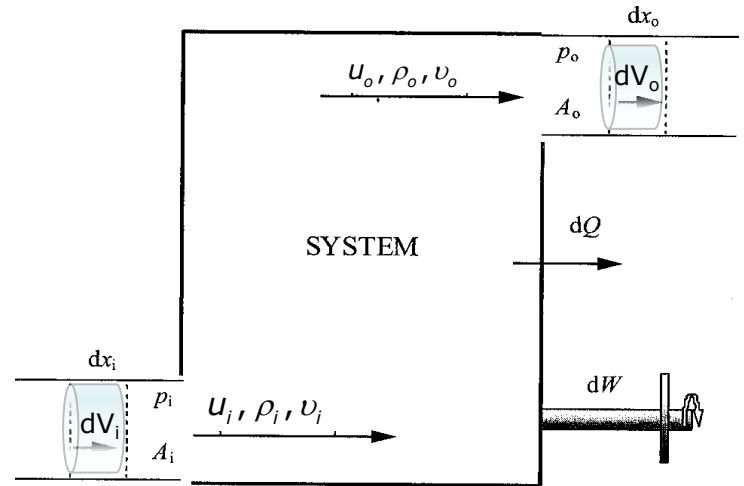incoming $\quad dU_i = u_i \cdot (A_i dx_i) + p_i \cdot (A_i dx_i) + \frac{1}{2}\rho_i v_i^2 \cdot (A_i dx_i)$

outgoing $\quad dU_o = u_o \cdot (A_o dx_o) + p_o \cdot (A_o dx_o) + \frac{1}{2}\rho_0 v_o^2 \cdot (A_o dx_o)$

Mass conservation :
$$dM_i = (\rho\, A\, v)_i = (\rho\, A\, v)_o = dM_o$$

Additional mechanical work output dW, heat output dQ

$$\frac{dE}{dt} = \frac{d(U_{in} - U_{out})}{dt} - \left(\frac{dW}{dt} + \frac{dQ}{dt}\right) \quad Steady\ state: \frac{dE}{dt} = 0$$

Power ∝ Fuel Flow

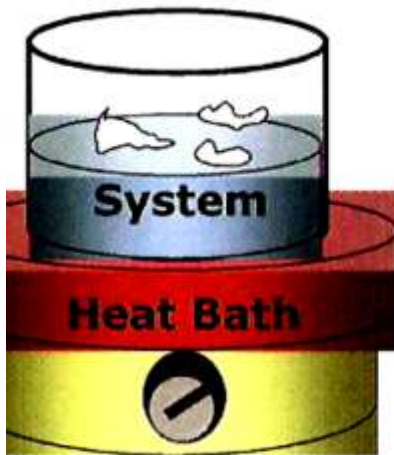$$\frac{dW}{dt} + \frac{dQ}{dt} \approx \frac{dW}{dt} = \left(h_i + \frac{1}{2}\rho_i v_i^2\right) A_i\, v_i - \left(h_o + \frac{1}{2}\rho_o v_o^2\right) A_o\, v_o$$

$$\frac{dW}{dt} \approx \left\{\left(\frac{h_i}{\rho_i} + \frac{v_i^2}{2}\right) - \left(\frac{h_o}{\rho_o} + \frac{v_o^2}{2}\right)\right\} \frac{dM}{dt}$$

↳ well insulated

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Spontaneous Reactions Require Free Energy

System in contact with an external energy donor ("Heat Bath" @ T=const.).
Bath can provide work-equivalent heat q_{surr} at no "cost" (T= const.) converted into **non-trivial (non-pV)** work

$$W_{total} = W_{pv} + W_{extra} \text{ (chemical rxn, melting, electric, ...)}$$

Consider isothermal reaction $1 \rightarrow 2$ at T, p = const.:
When is $\Delta S_{1\rightarrow 2} > 0$ (spontaneous) and produces W_{extra}?

$$\left(\Delta S - \frac{q}{T}\right)_{1\rightarrow 2} \geq 0 \ (= \text{for reversible}) \qquad q = \Delta U - w(:= w_{pV})$$
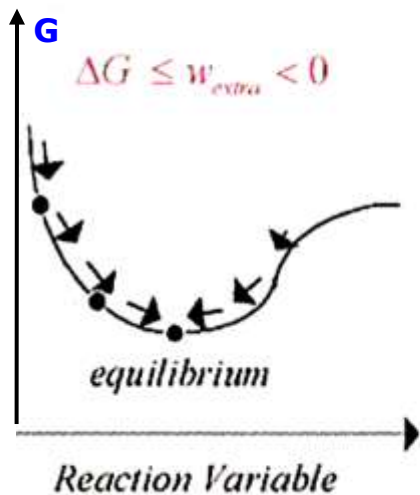
$$T \cdot \Delta S \geq \left[\Delta U - w\right]_{1\rightarrow 2} = \left[U_2 - U_1 - \left(-p \cdot (V_2 - V_1)\right)\right] = H_2 - H_1$$

$$T \cdot \Delta S \geq \Delta H \ \rightarrow \ \Delta G := \Delta(H - T \cdot S) \leq 0 \quad \Delta G = 0 \ \text{for reversible}$$

$\Delta G \leq w_{extra} < 0$

Thermodynamic Potentials

Gibbs Free Energy $\mathbf{G = H - T \cdot S}$ $(p, T : const)$

Helmholtz Free Energy $\mathbf{F = U - T \cdot S}$ $(T : const)$

$$\Delta G = \Delta(H - T \cdot S) = \Delta H - T \cdot \Delta S = (\Delta U + p \cdot \Delta V) - T \cdot \Delta S$$

$$= \left(q_{rev} + w_{pV} + w_{extra} + p \cdot \Delta V\right) - \underbrace{T \cdot \Delta S}_{\geq q_{rev}} \leq w_{extra} \leq 0$$

equilibrium

Reaction Variable

Maximum non-pV work system can do: $\mathbf{W_{extra} = \Delta G < 0}$

Thermodynamics: Phenomenology & Applications

- Work and other forms of energy

- Fundamental Laws of Thermodynamics

- Ideal-gas laws and simple processes

    Technological applications, cyclic engines

    Carnot process

- **Real gases equation of state**

    Technological applications

- Phase equilibria, solutions

- Transport phenomena

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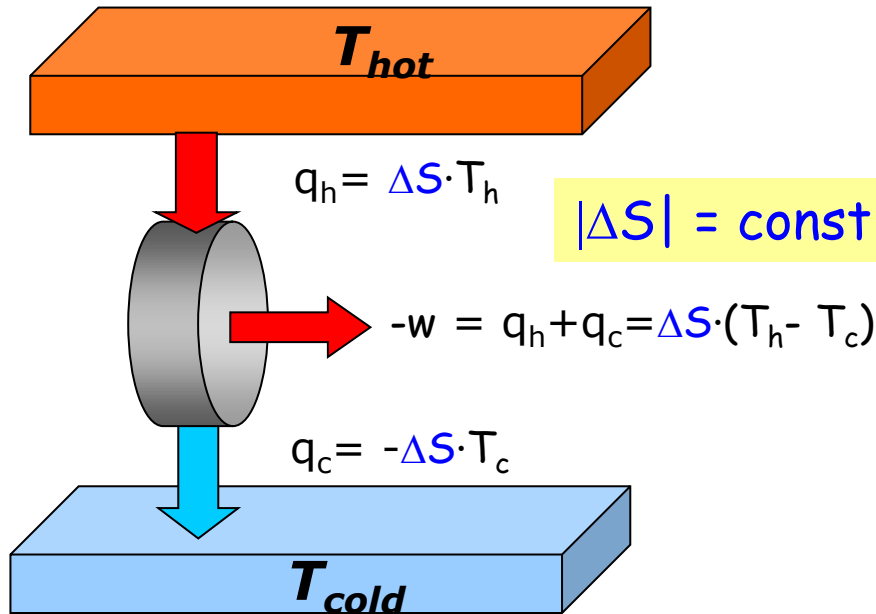
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$$\varepsilon_C = \frac{-w}{q_h} = \frac{q_h + q_c}{q_h}$$

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

$$Process\ at\ p,T = const. \xrightarrow{U = const} q = \Delta H \to$$

$$w = -(T_h - T_c) \cdot \Delta S = -\left(\frac{T_h - T_c}{T_h}\right) T_h \cdot \Delta S$$

$$= -\left(\frac{T_h - T_c}{T_h}\right) \Delta H (T_h) = -\underbrace{\Delta(H - T \cdot S)}_{=\Delta G}$$

In practice, T_h of heat bath depends on fuel heating value (max temperature T_{ad}).
Transfer from fuel to heat reservoir: $\varepsilon_F = (T_{ad} - T_h)/(T_{ad} - T_c)$

→ Effective Carnot efficiency: $\varepsilon = \varepsilon_C \cdot \varepsilon_F = \left(1 - \frac{T_c}{T_h}\right) \cdot \left(\frac{T_{ad} - T_h}{T_{ad} - T_c}\right)$