

Thermodynamics: Phenomenology

- Work and other forms of energy
 - Transfer and dissipation
- 1. & 2. Fundamental Laws of Thermodynamics
- Ideal-gas laws and simple processes
 - Technological applications, cyclic engines
- Free energy in chemical reactions
- Real gases equation of state
 - Technological applications
- Phase equilibria
- Kinetic theory of gases

Reading Assignments

Weeks 13&14

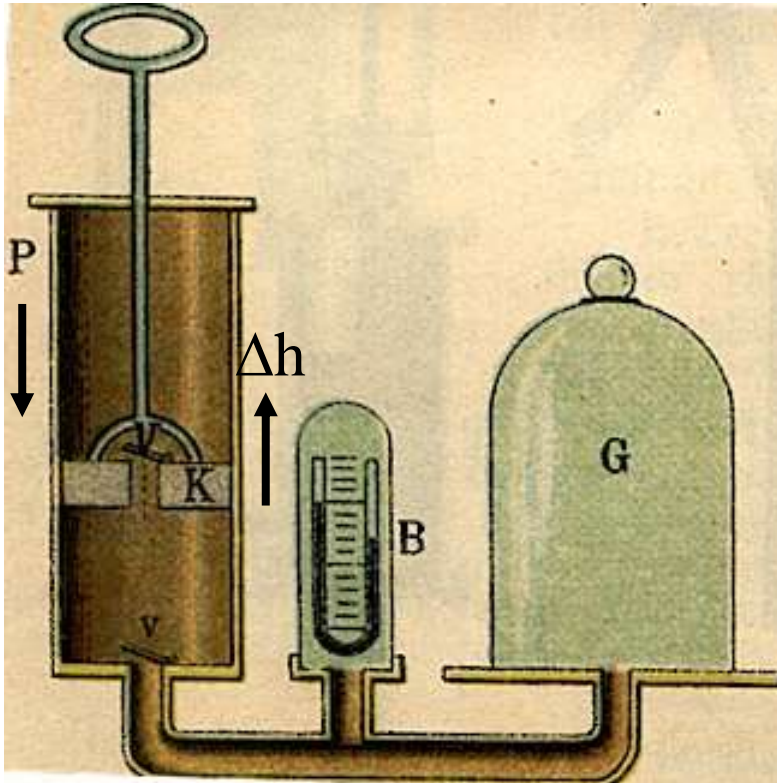
LN V-VI:

Section IG Free Energy

Kondepudi Ch. 6 & 7
Additional Material

McQuarrie & Simon
Ch. 7 & 8

Ideal-Gas Laws: Simple Processes



Compression of a gas volume, at pressure equilibrium,

$$P = P_{ext} = \text{atmospheric pressure}$$

$$P = F / A = P_{ext}$$

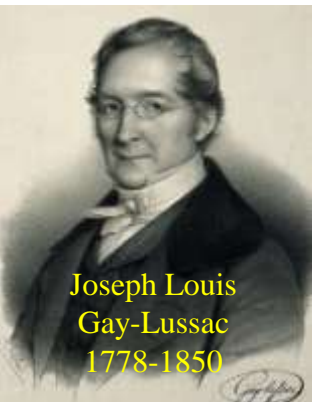
$$w = -F \cdot \Delta h = -P \cdot \Delta V$$

$\Delta V > 0$: *Expansion*;

$\Delta V < 0$: *Compression*

Sign Convention: Work is counted positive ($w > 0$) when it increases the internal energy U of a gas.

Gas Laws: Ideal-Gas Equation of State EoS



Robert Boyle, Guillaume Amontons, Gay-Lussac
Response of dilute gases of specified amounts (#moles = n ,
Avogadro)

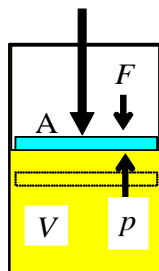
Boyle's Law $P(V) \propto 1/V$ or $P \cdot V = \text{const}(n, T)$

Amontons' (Gay – Lussac's) Law $P(T) = P(0) \cdot [1 + \alpha \cdot T_c] \propto T$

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

$\alpha \approx 3.66 \cdot 10^{-3}/^\circ C \approx 1/273^\circ C \rightarrow$ 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

$$P \cdot V = n \cdot R \cdot T = N \cdot k_B \cdot T$$

$$P = \rho \cdot k_B \cdot T$$

Dalton's Law partial pressures $P = \sum_i P_i$

Amontons' Paper and Setup

DES SCIENCES. 155

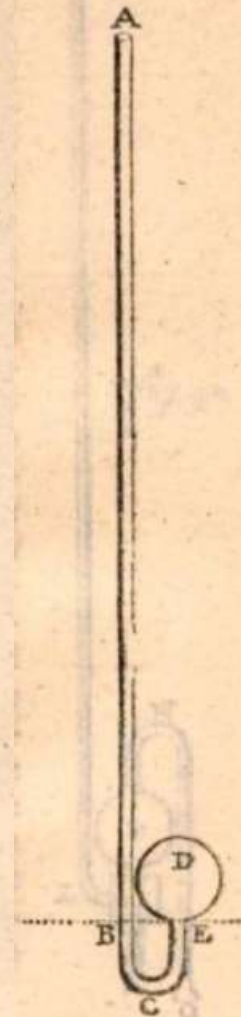
DISCOURS SUR QUELQUES

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

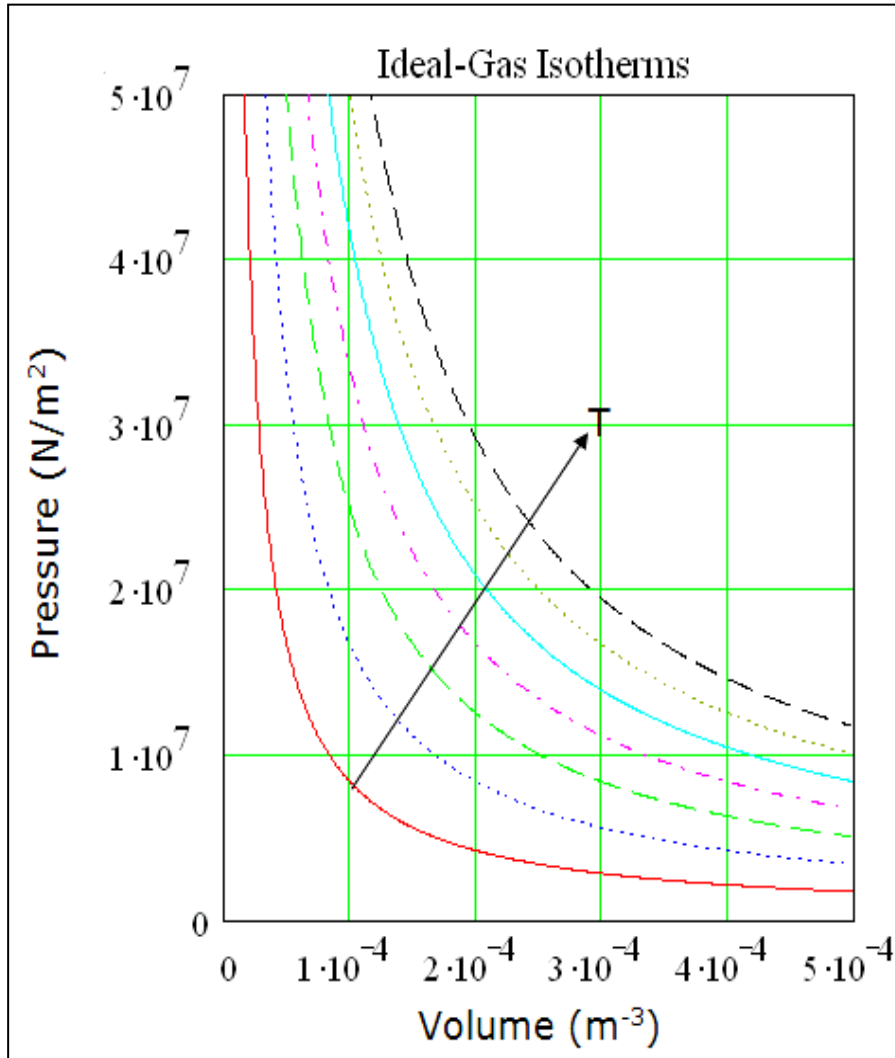
PAR M. AMONTONS.

LEs expériences qui peuvent conduire à connoître la nature de l'air dans lequel nous vivons, sont d'une conséquence assez considérable pour mériter qu'on y fasse une particulière attention. Celles que je fis il y a trois ans sur la dilatation de l'air par la chaleur de l'eau bouillante, me firent connoître que des masses inégales d'air chargées de mêmes poids ou de poids égaux, augmentoient également la force de leur ressort 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 ressort de l'air au-dessus de ce qu'il en conserve dans l'eau que nous appellons froide, ces expériences me portèrent pour lors à croire que ce n'étoit que d'une quantité capable de soutenir dix pouces en hauteur de mercure outre le poids de l'atmosphère: mais ayant depuis poussé plus loin ces expériences, j'ai trouvé que le ressort de l'air augmenté par la chaleur de l'eau bouillante n'étoit pas fixé à ne soutenir seulement que dix pouces de mercure plus que la charge de l'atmosphère; mais qu'il en soutenoit plus ou

1701.
28. Juin.



Ideal-Gas Equation of State EoS



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**.

$$P \cdot V = n \cdot R \cdot T = N \cdot k_B \cdot T$$

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

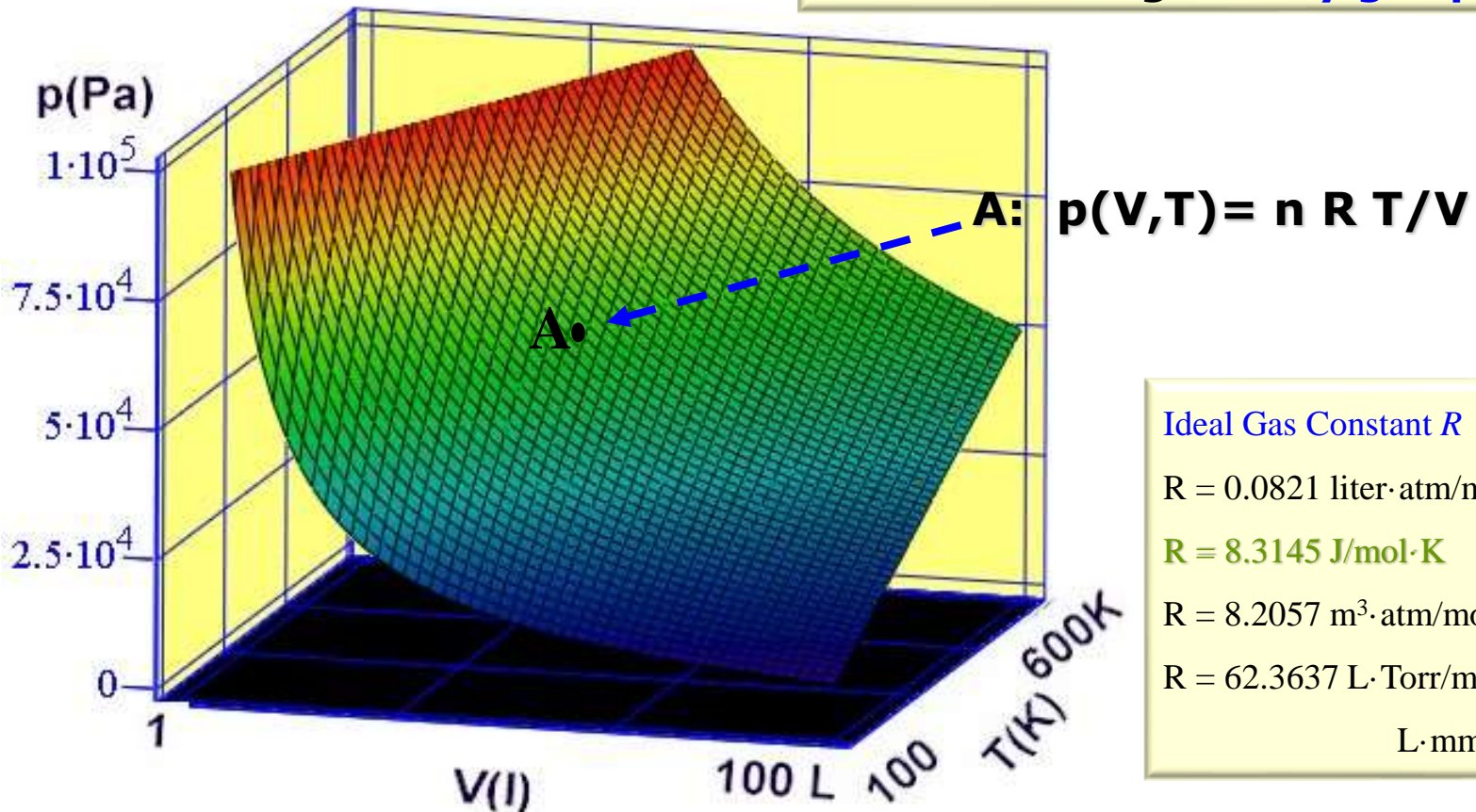
Idealization: At $T=0$: $P = 0$, $V = 0$.
Idealization not viable at $T=0$ high
high matter density \rightarrow particles interact

Gas Constant $R = 8.31451 \text{ J}/(\text{K} \cdot \text{mole})$
Boltzmann Constant $k_B = 1.38 \cdot 10^{-23} \text{ J}/\text{K}$

The (Ideal-Gas) Equation of State

Ideal-Gas EOS

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



Ideal Gas Constant R

$R = 0.0821 \text{ liter} \cdot \text{atm} / \text{mol} \cdot \text{K}$

$R = 8.3145 \text{ J} / \text{mol} \cdot \text{K}$

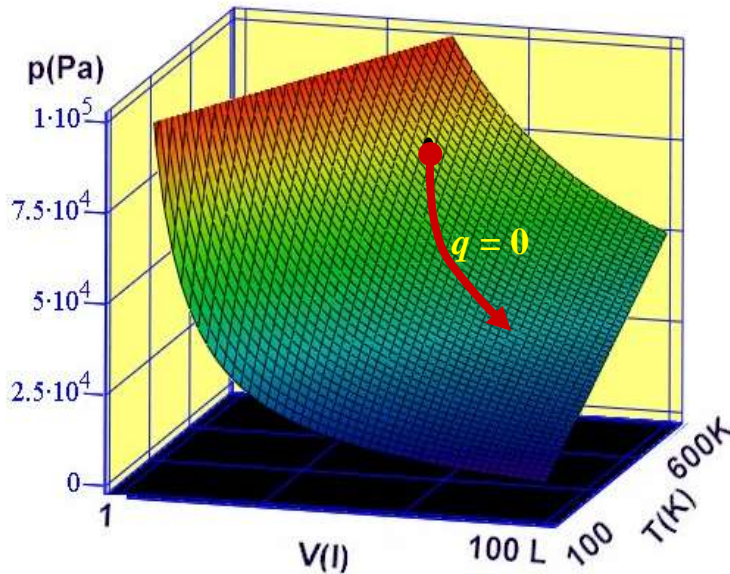
$R = 8.2057 \text{ m}^3 \cdot \text{atm} / \text{mol} \cdot \text{K}$

$R = 62.3637 \text{ L} \cdot \text{Torr} / \text{mol} \cdot \text{K}$ or

$\text{L} \cdot \text{mmHg} / \text{mol} \cdot \text{K}$

State functions p, V, T, \dots . 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



Relation between internal energy of ideal gas and pressure-volume relation.

Adiabatic expansion means (here) no exchange of heat energy, $dq = 0$.

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

Calculation for 1 mole *ideal gas*

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

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

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

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

$$\gamma = \frac{C_P}{C_V}; \quad \frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0$$



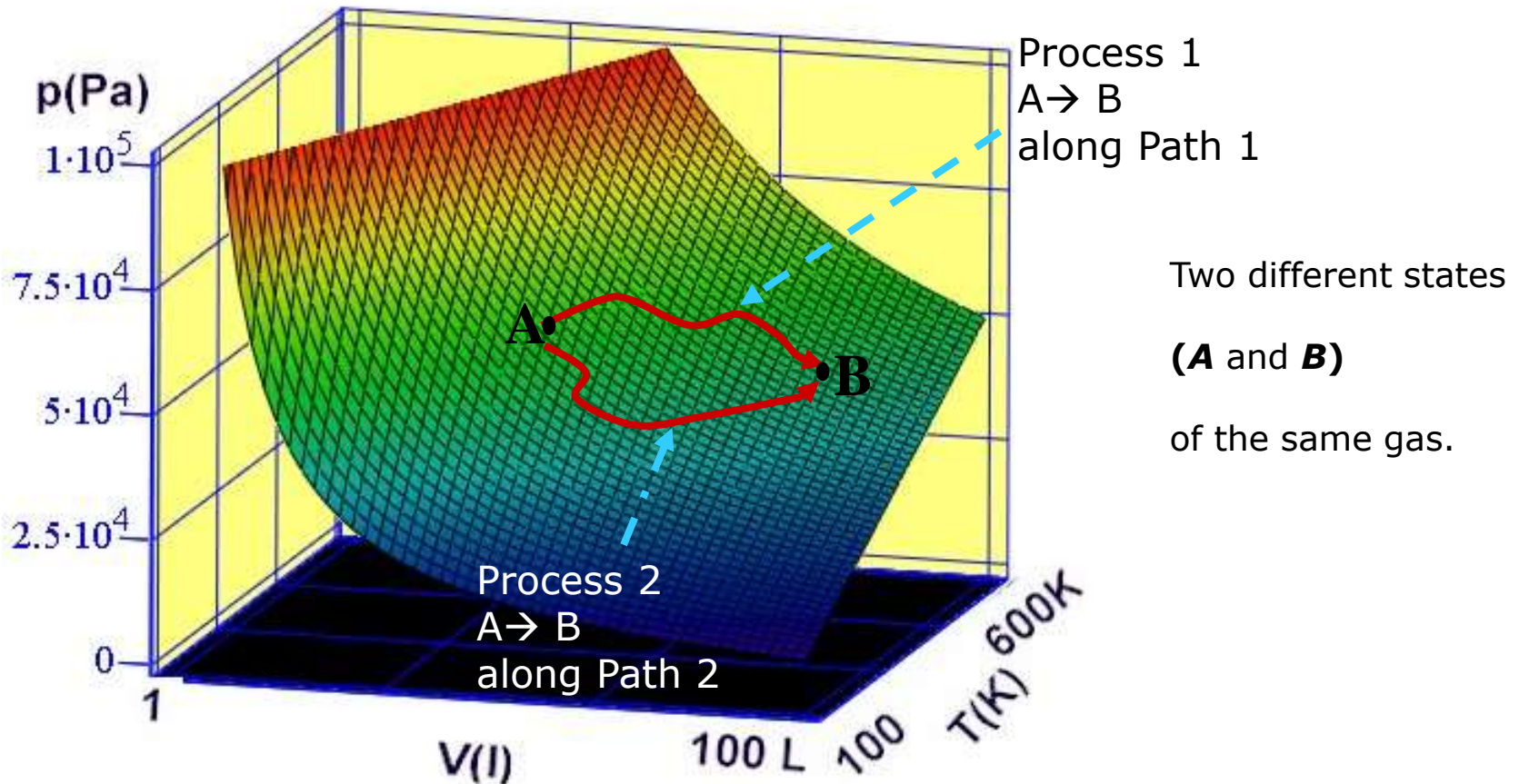
$$\begin{aligned} T \cdot V^{\gamma-1} &= \text{const.} \\ p \cdot V^\gamma &= \text{const.} \\ T^\gamma \cdot p^{1-\gamma} &= \text{const.} \end{aligned}$$

Pressure Units

V · T · E	pascal	bar	technical atmosphere
	Pa	bar	at
1 Pa	$\equiv 1 \text{ N/m}^2$	10^{-5}	1.0197×10^{-5}
1 bar	10^5	$\equiv 10^6 \text{ dyn/cm}^2$	1.0197
1 at	0.980665×10^5	0.980665	$\equiv 1 \text{ kp/cm}^2$
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}

Transitions Between States

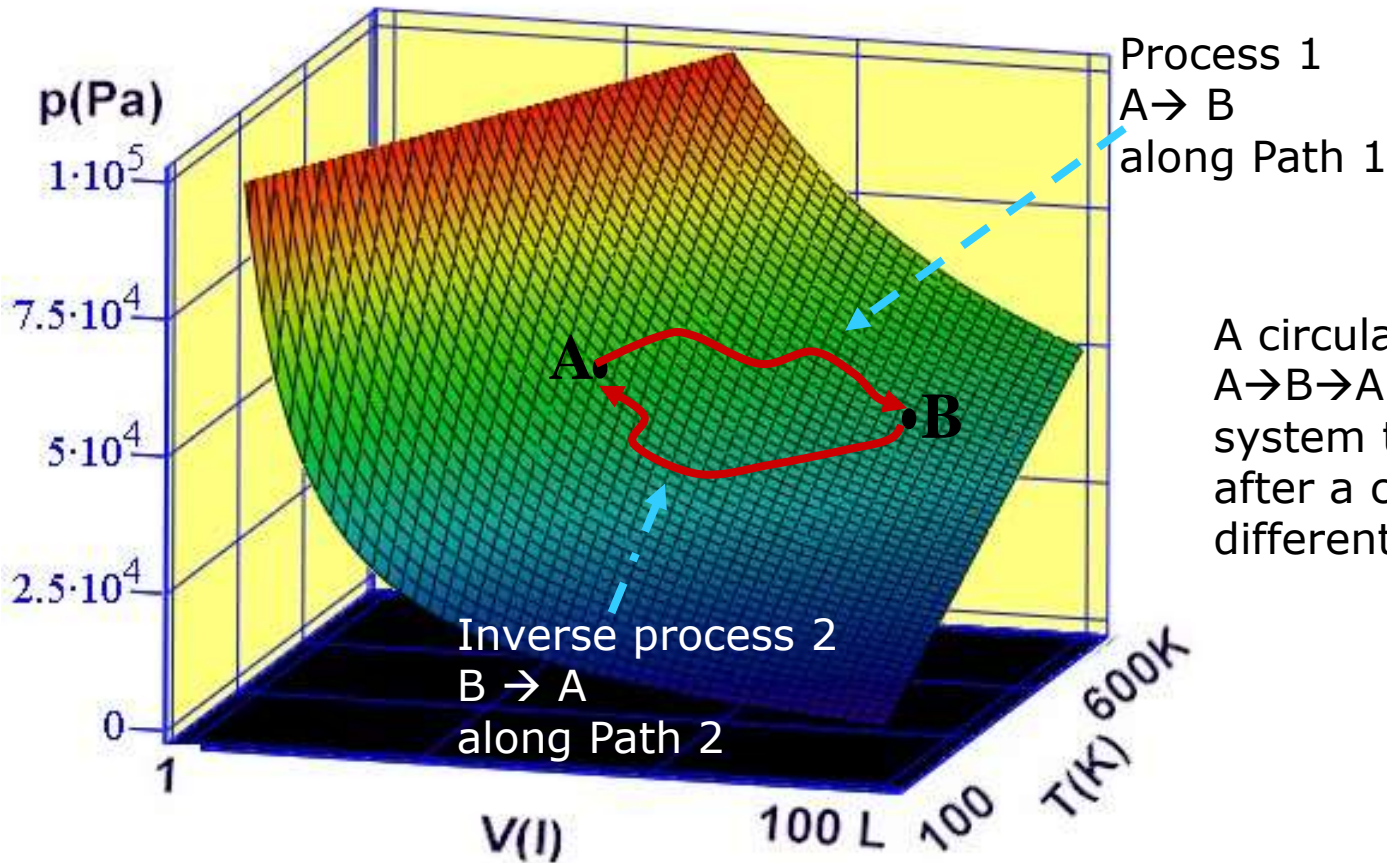
Ideal-Gas EOS



State functions p , V , T ,... describe the system states **but not the processes** connecting states. **Two states A, B can be reached by different processes representing different pathways on the $\{p, V, T\}$ hyperplane.** The two processes $A \xrightarrow{1} B$ and $A \xrightarrow{2} B$ differ by different relative amounts of energy transfer via absorption of heat and work.

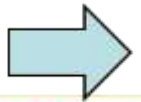
A Circular Process Connecting 2 States

Ideal-Gas EOS



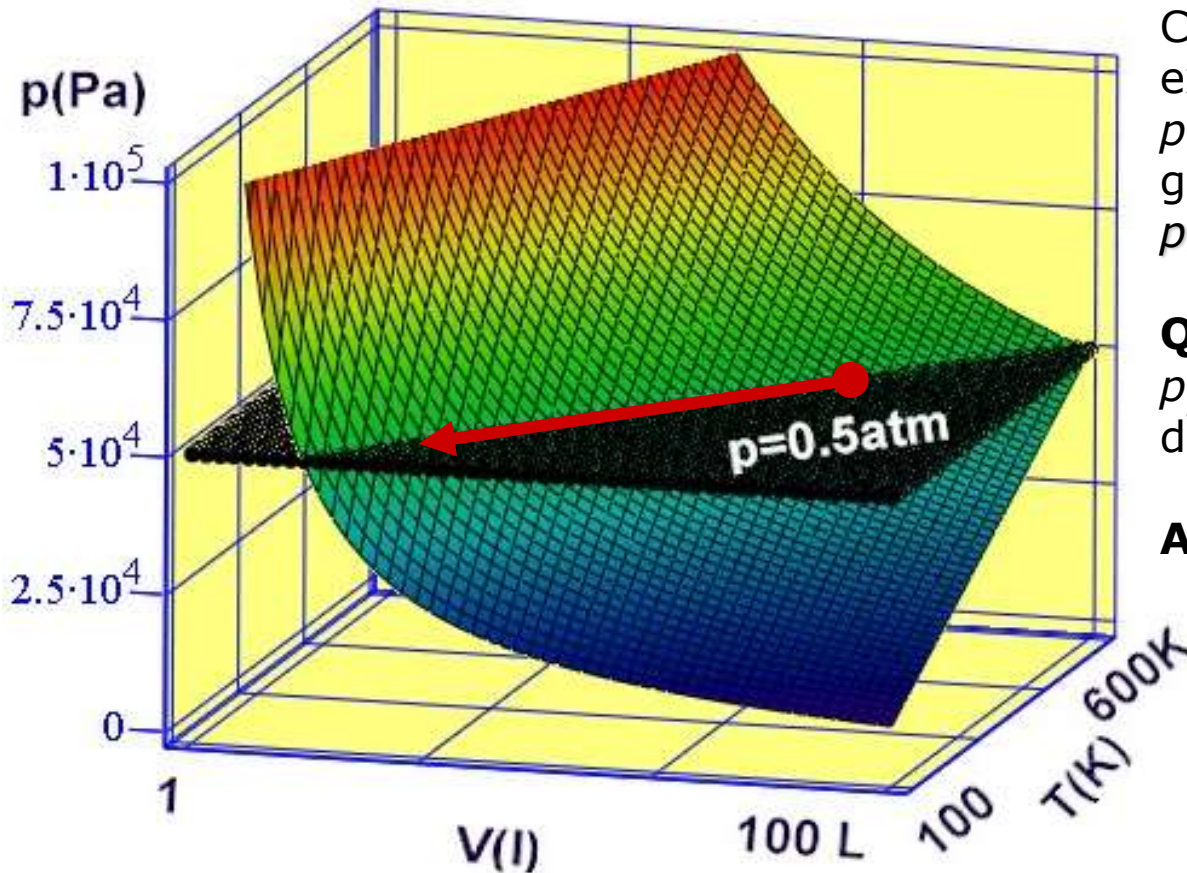
A circular process $A \rightarrow B \rightarrow A$ returns the system to its initial state after a combination of different processes.

In reversible processes, system and surroundings may do different amounts of work and absorb different amounts of heat. Cyclic processes based on this principle can exchange different forms of energy between system and surroundings, e.g., system can do work in exchange of absorbing heat.



Specific Elements

Isobaric Compression



Compression by constant external force (pressure p_{ext}) in equilibrium with gas pressure, $p = p_{gas} = p_{ext}$.

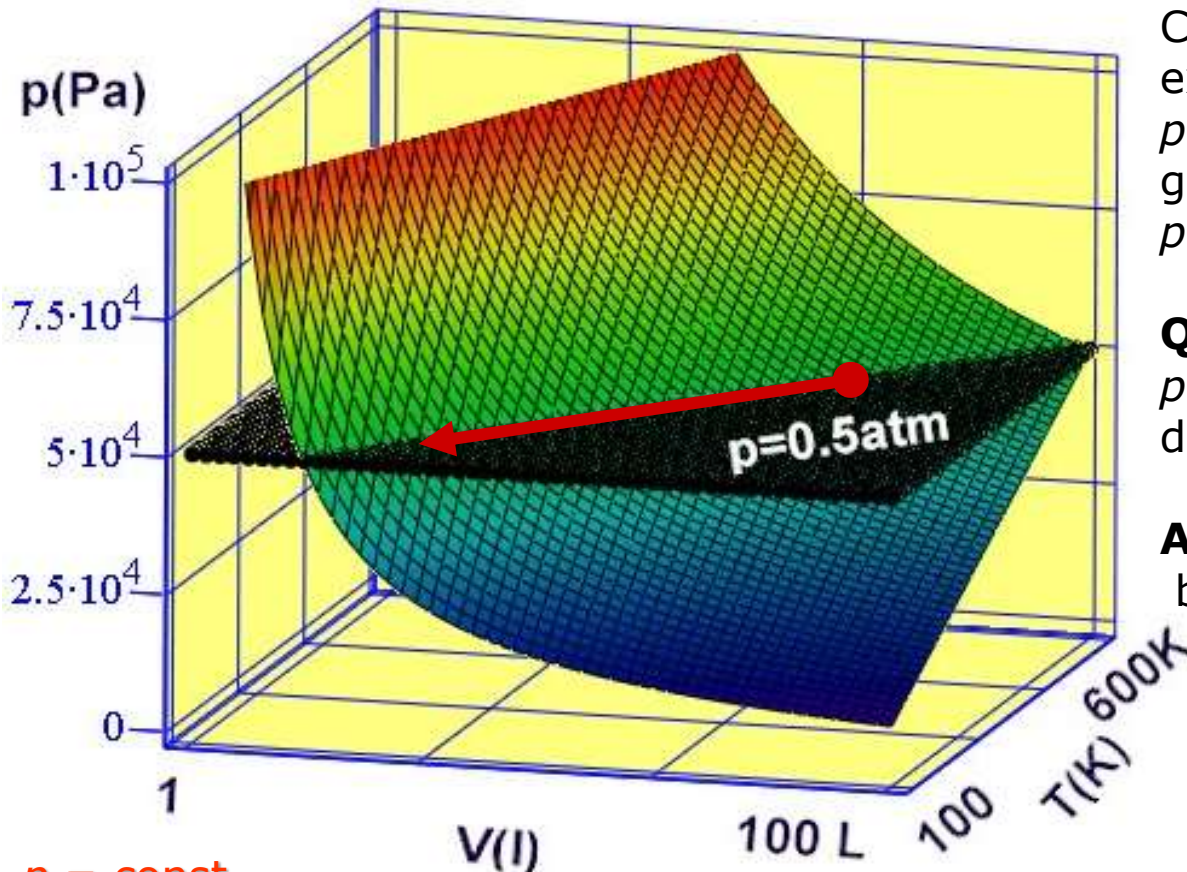
Q: How can pressure $p = p_{gas}$ be kept constant during compression?

A: ??

Isobaric Compression

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Phen_Process



Compression by constant external force (pressure p_{ext}) in equilibrium with gas pressure, $p = p_{gas} = p_{ext}$.

Q: How can pressure $p = p_{gas}$ be kept constant during compression?

A: Gas has to be cooled but $p \cdot V = R \cdot T$ ($n=1$)

→ Use EOS to calculate how much cooling is needed.

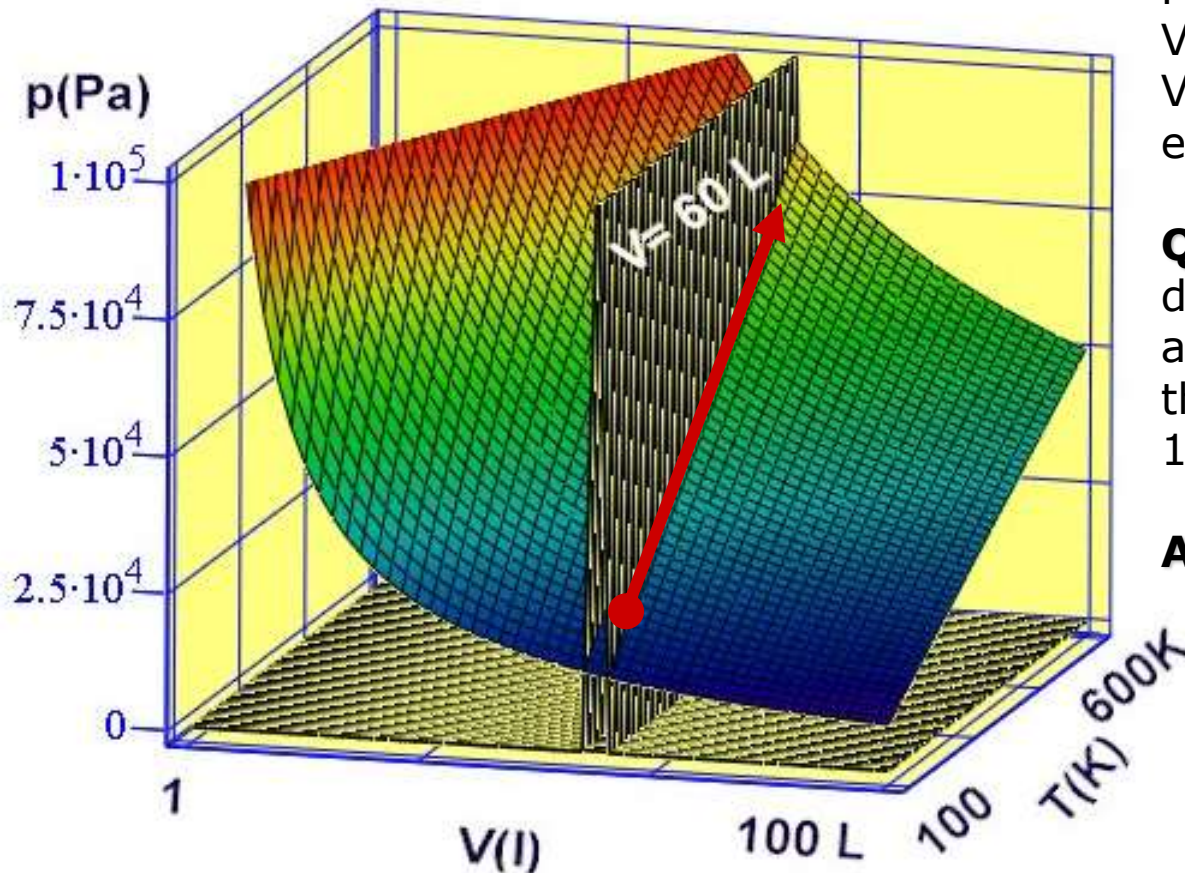
$p = \text{const.}$

$$\frac{\Delta(p \cdot V) = p \cdot \Delta V = \Delta(R \cdot T) = R \cdot \Delta T}{p \cdot V = R \cdot T}$$

$$\rightarrow \frac{\Delta(pV)}{pV} = \frac{\Delta V}{V} = \frac{\Delta T}{T} = \frac{\Delta U}{U} < 0$$

↙ q

Isochoric ($\Delta V = 0$) Pressurization

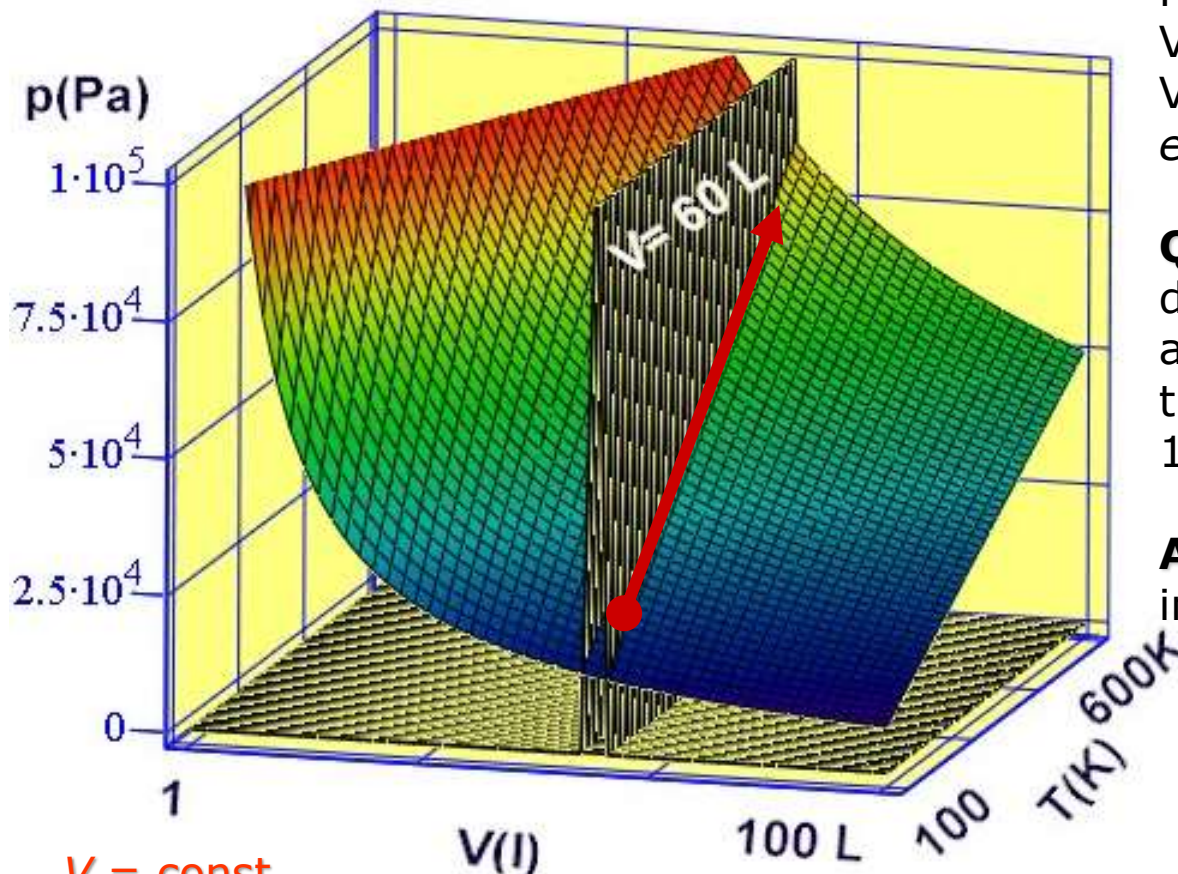


Pressurization at constant V is not associated with p - V work, but the internal energy U changes.

Q: How and by how much does the internal energy of a gas cylinder change in the pressurization by 10%?

A: ??

Isochoric ($\Delta V = 0$) Pressurization



Pressurization at constant V is not associated with p - V work, but the internal energy U changes.

Q: How and by how much does the internal energy of a gas cylinder change in the pressurization by 10%?

A: By heating to 110% of initial T .

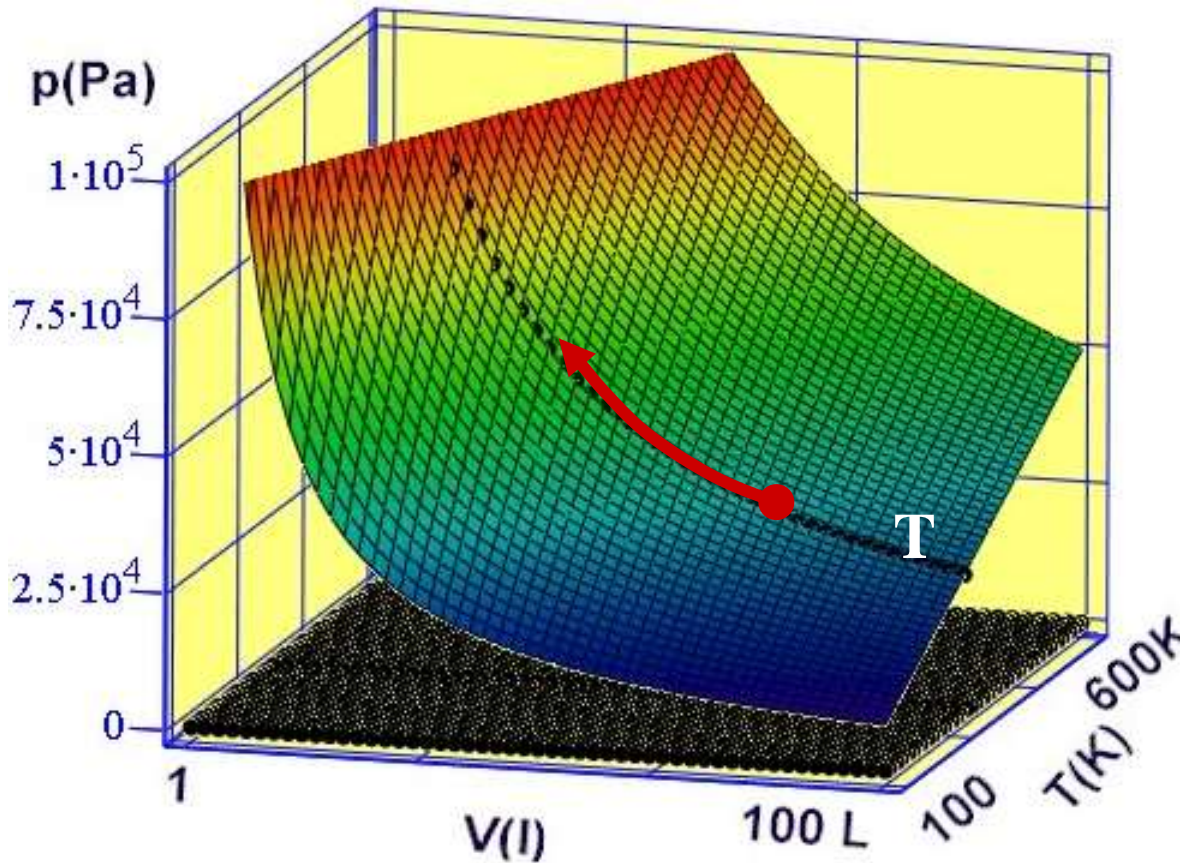
$V = \text{const.}$

$$\frac{\Delta(p \cdot V) = (\Delta p) \cdot V = \Delta(R \cdot T) = R \cdot \Delta T}{p \cdot V = \quad = R \cdot T}$$

$$\rightarrow \frac{\Delta(pV)}{pV} = \frac{\Delta p}{p} = \frac{\Delta T}{T} = \frac{\Delta U}{U} > 0$$



Isothermal Compression

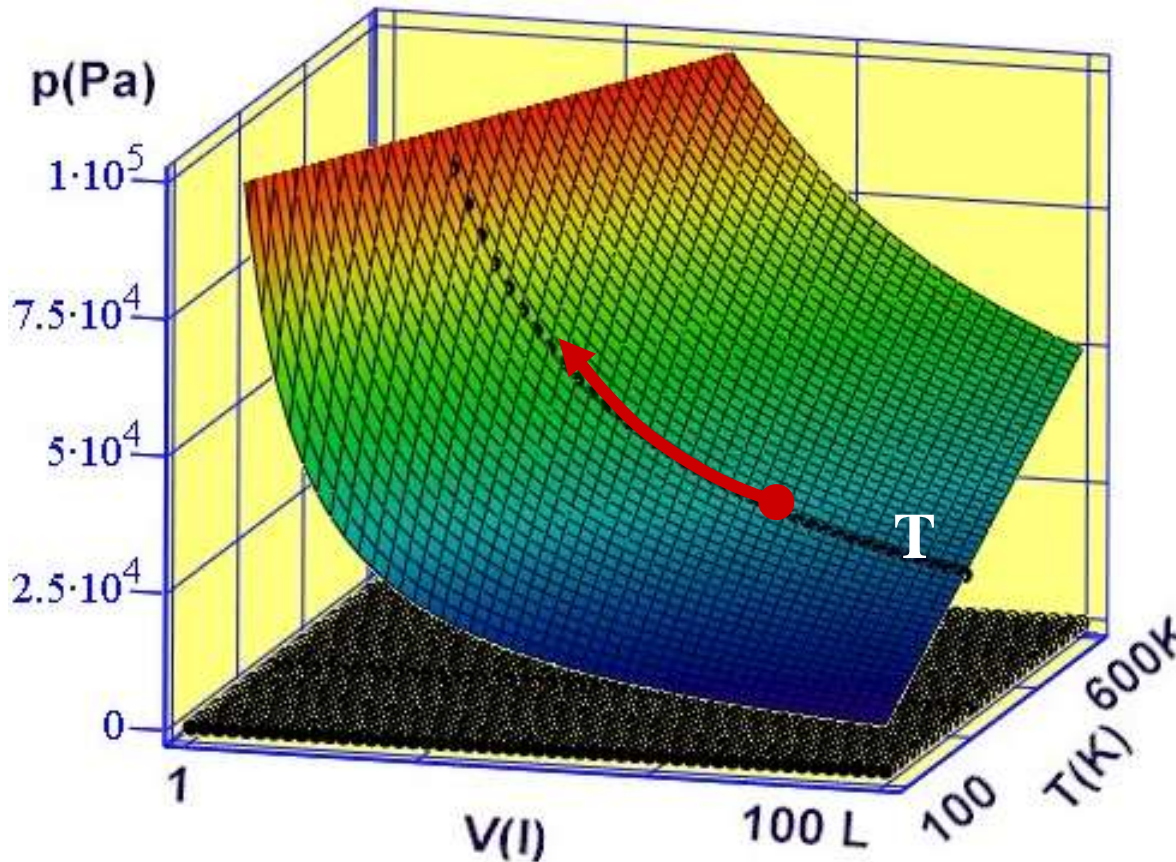


Compression by external force in equilibrium with varying gas pressure, $p(V) \neq \text{const.}$, with constant temperature $T = \text{const.}$

Q: How can the temperature be kept constant when work is done on the gas, in a compression?

A: ???

Isothermal Compression

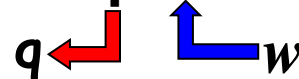


Compression by external force in equilibrium with varying gas pressure, $p(V) \neq \text{const.}$, with constant temperature $T = \text{const.}$

Q: How can the temperature be kept constant when work is done on the gas, in a compression?

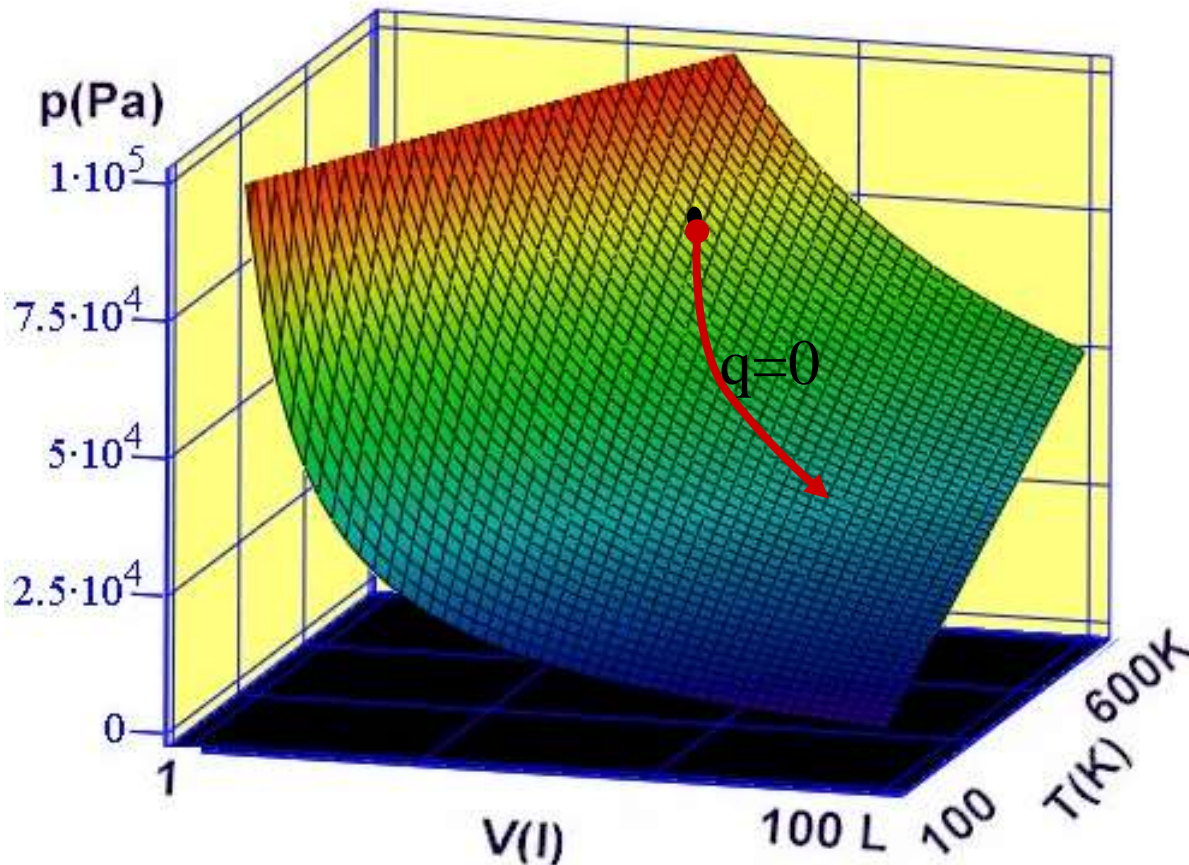
A: Isothermal compression does not increase the internal energy. Applied work must be counterbalanced by emission of heat (cooling).

$$\text{For } \mathbf{q} = -\mathbf{w}, \rightarrow \Delta \mathbf{U} = \mathbf{q} + \mathbf{w} = \mathbf{0}. \rightarrow \text{can be } \Delta \mathbf{S} = \mathbf{0}$$



Adiabatic (Isentropic, $q=0$) Expansion

$$q = 0 \rightarrow dS = 0 \rightarrow T \cdot V^{\gamma-1} = \text{const.}; \quad \gamma = \frac{c_p}{c_v}$$



Expansion against an external force $F (\neq, =0)$ in equilibrium with varying gas pressure, $p(V) \neq \text{const.}$,
no exchange of heat energy, $q = 0$.

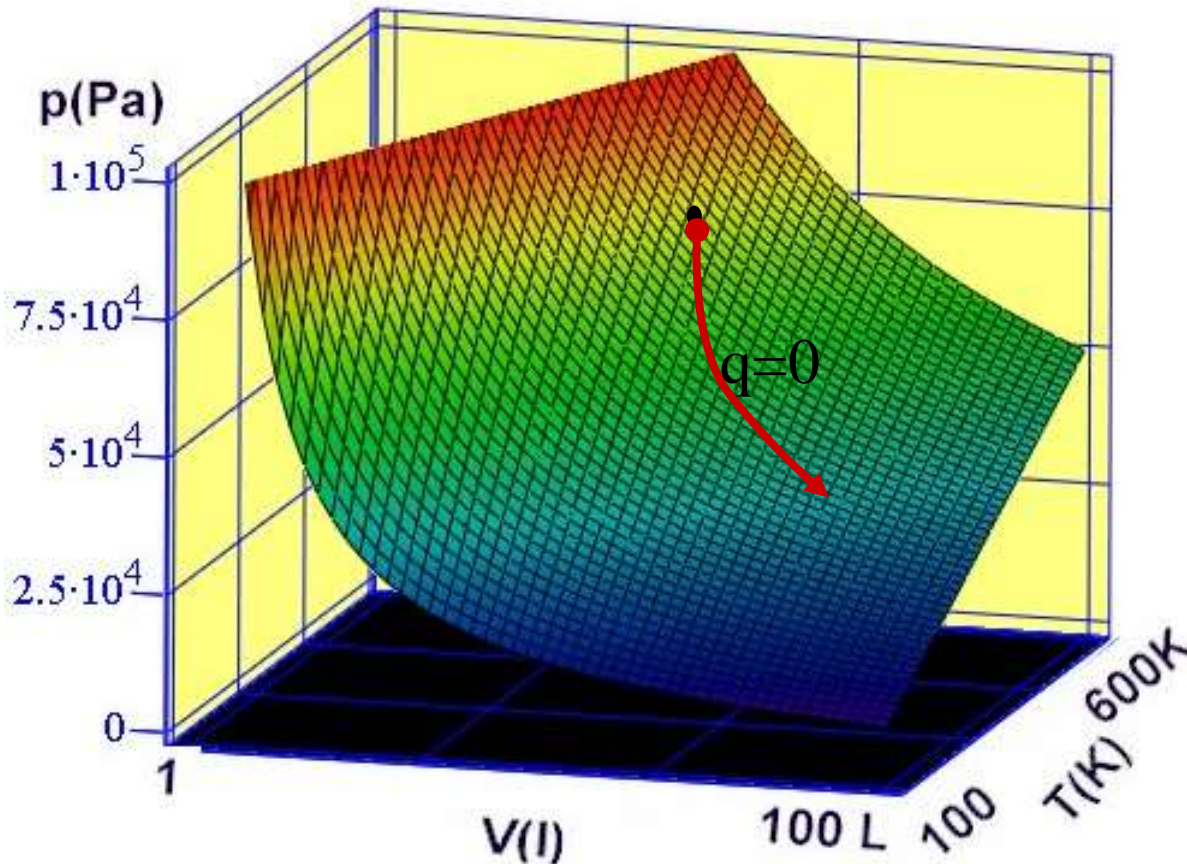
Q: How does the internal energy change?

A: If work $w = 0$,.....

If $w \neq 0$,

Adiabatic (Isentropic, $q=0$) Expansion

$$q = 0, dS = 0 \rightarrow T \cdot V^{\gamma-1} = \text{const.}; \quad \gamma = \frac{C_p}{C_v}$$



Expansion against an external force $F (\neq, =0)$ in equilibrium with varying gas pressure, $p(V) \neq \text{const.}$,
no exchange of heat energy, $q = 0$.

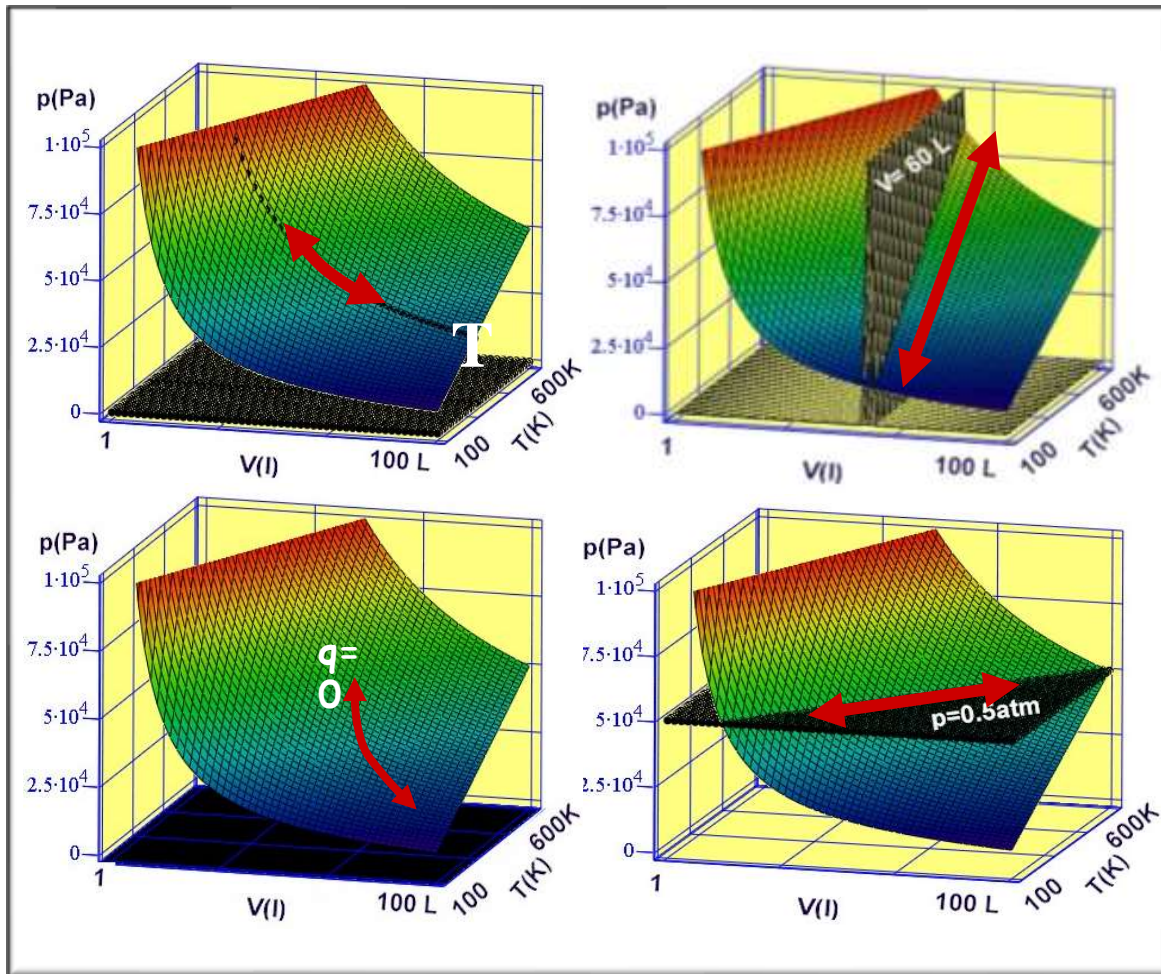
Q: How does the internal energy change?

A: If $F=0 \rightarrow$ work $w = 0$ (in addition to $q = 0$), $\rightarrow \Delta U = 0$, i.e.,

$U = \text{const.}$, and therefore $T = \text{const.}$ (but $\Delta p < 0$ & $\Delta V > 0$)

If $w \neq 0$, then $\Delta U = q + w = w$ and $\Delta U = C_v \cdot \Delta T = w < 0 \rightarrow \Delta T < 0$. \rightarrow can be $\Delta S = 0$

Reversible Processes



Of interest for cyclic machines.

Slow equilibrium processes $A \rightarrow B$, subject to boundary conditions of:

1. $\Delta p = 0$ (isobaric)
2. $\Delta V = 0$ (isochoric)
3. $\Delta T = 0$ (isothermal)
4. $q = 0$ (adiabatic)

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

Reversibility is not guaranteed for all processes involving an ideal gas.

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Isobaric Compression

Compress 1 mole at $p = \text{const.}$

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

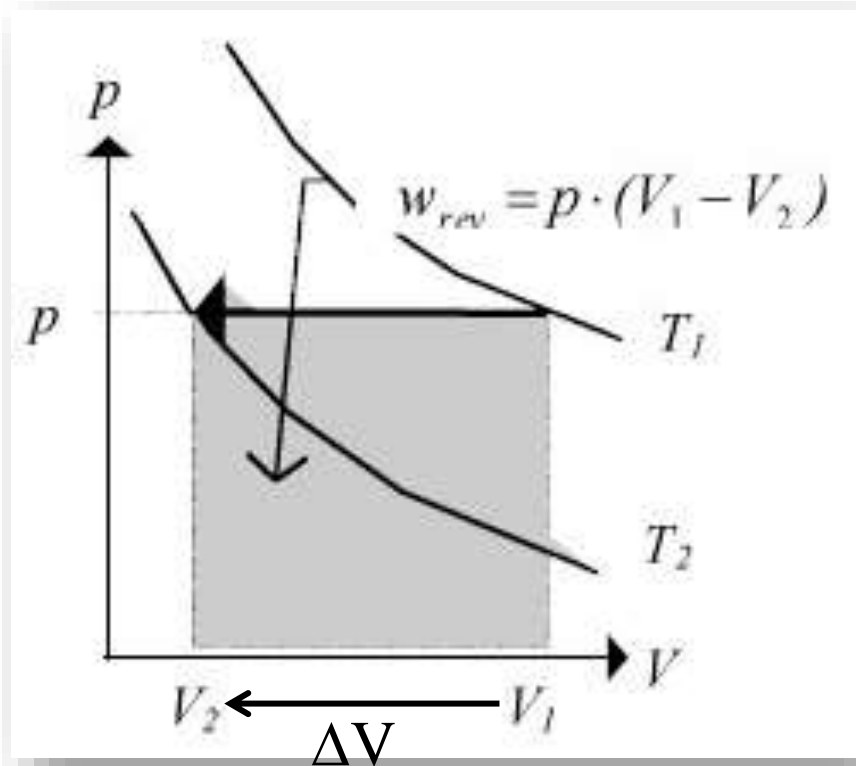
$$q = C_p \cdot \Delta T = \frac{5}{2} R \cdot \frac{p \cdot \Delta V}{R} = -\frac{5}{2} w < 0$$

Enthalpy change (for $p = \text{const.}$):

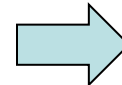
$$\Delta H = C_p \cdot \Delta T = C_p \cdot [T_2 - T_1] = q < 0$$

= emitted heat (internal energy)

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



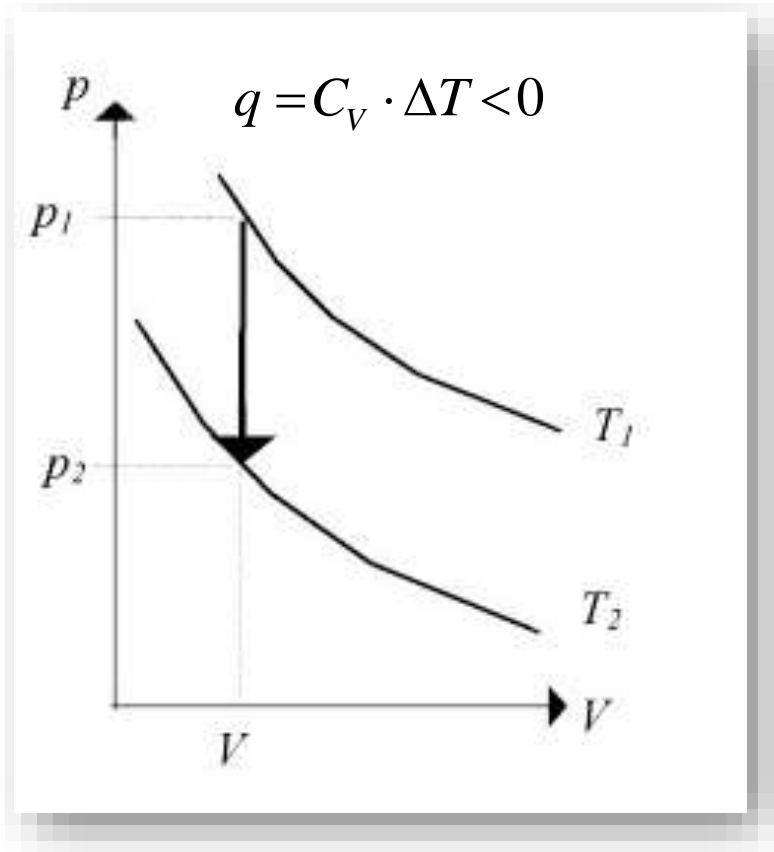
Internal energy change



$$\Delta U = C_v \cdot [T_2 - T_1] < 0$$

Inverse process: **heating** gas by q at constant p , e.g., $p = p_{atm}$, leads to expansion, $V_2 \rightarrow V_1 > V_2 \rightarrow$ drives piston out $\rightarrow q = \Delta U - w = C_v \Delta T + R \Delta T = C_p \Delta T$.

Decompression



Isochoric ($V = \text{const.}$) decompression
 \rightarrow of 1 mole $w = -p\Delta V = 0$

Work done on system $w = 0$ ($\Delta V = 0$)

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

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

$$T_1^\gamma \cdot p_1^{1-\gamma} = T_2^\gamma \cdot p_2^{1-\gamma} \rightarrow p_2 = p_1 \left(\frac{T_1}{T_2} \right)^{\frac{\gamma}{1-\gamma}}$$

1. Law of Thermodynamics :

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

Enthalpy change

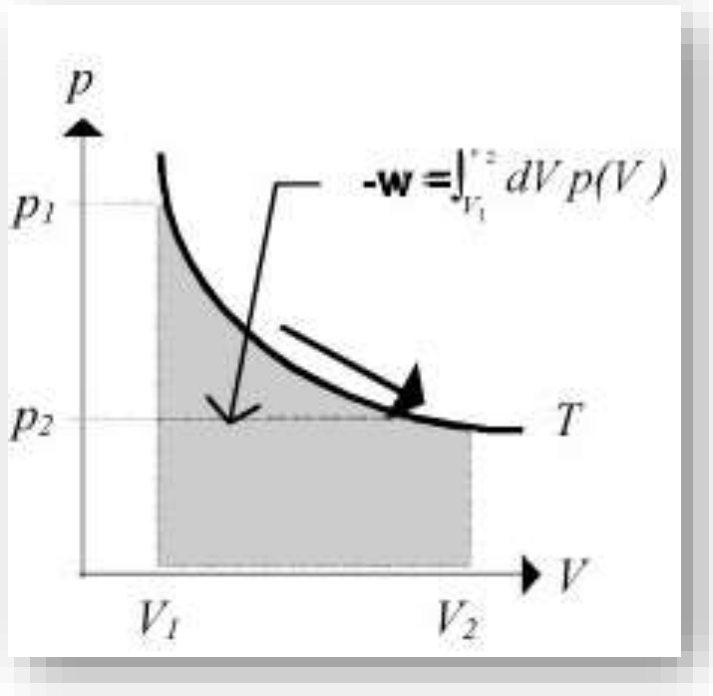
$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) = (C_V + R) \cdot \Delta T \\ &= C_p \cdot [T_2 - T_1] \quad (\text{always} = C_p \cdot \Delta T) \end{aligned}$$

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

Inverse process: heating at constant V , leads to increased temperature and pressure. Use adiabatic EoS to evaluate.

Isothermal Expansion/Compression

Internal energy U of ideal gas $U = \text{function of } T \text{ alone}$



$w = - \text{area under curve } p(V)$

Total work (1 \rightarrow 2):

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

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

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

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

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

1. LTD: $q = \Delta U - w = -w$
=0

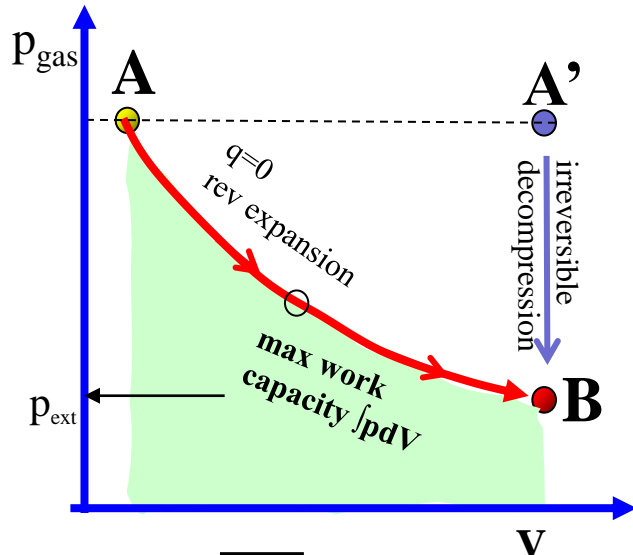
$$q = -R \cdot T \cdot \ln \left(\frac{V_1}{V_2} \right) > 0$$

$$T \cdot \Delta S = \cancel{\Delta U} + p \Delta V = R \cdot T \cdot \ln \left(\frac{V_2}{V_1} \right) > 0$$

System: entropy gain $\Delta S = R \cdot \ln \left(\frac{V_2}{V_1} \right) = \frac{q}{T} > 0$

In isothermal expansion, system absorbs heat and increases entropy.

Work/Heat in Reversible vs. Irreversible Processes



System interacts thermally with environment, Equilibrium: $\Delta T=0 \rightarrow$ path on an isotherm.

In gentle process $A \rightarrow B$, system always at equilibrium (e.g, $p_{\text{ext}} dV = p_{\text{gas}} dV + q$), system produces maximum work. (balance by *including the -sign, sign convention!*):

$$w_{\text{rev}} < w_{\text{irrev}} < 0 \rightarrow |w_{\text{rev}}| > |w_{\text{irrev}}|$$

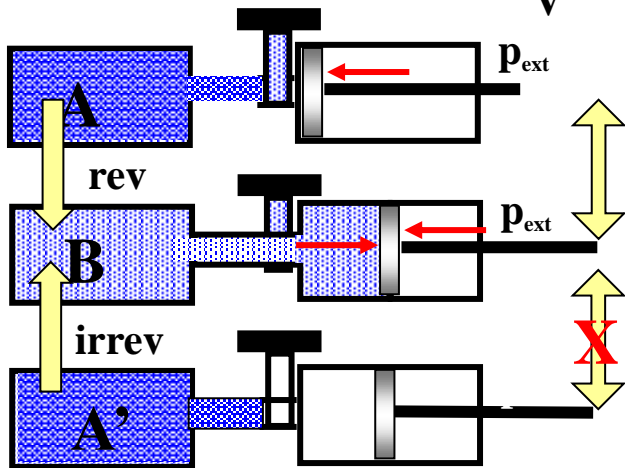
Where did the difference Δw go? Nowhere!
Also less/no heat exchanged on irreversible path.

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

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

$$\rightarrow w_{\text{rev}} < w_{\text{irrev}} \leftrightarrow q_{\text{rev}} > q_{\text{irrev}} = 0$$

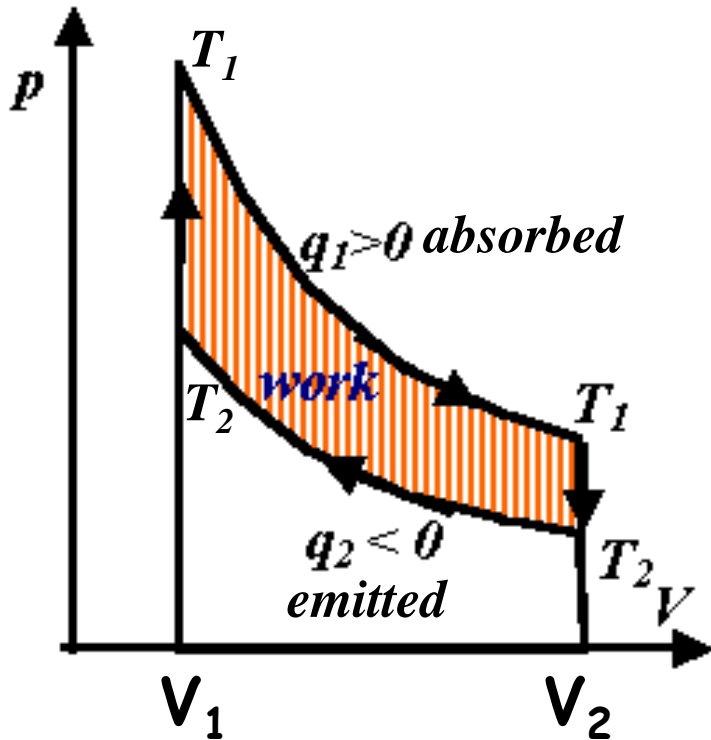
The largest (negative) amount w_{rev} is delivered in reversible process $\rightarrow q_{\text{rev}}$ is largest amount of heat system can absorb reversibly and convert into work.



Opening valve @ $t_0 \rightarrow$ Expansion

Irreversible, spontaneous processes: Inefficient conversion of energy to useful work.

Expansion-Compression Cycles



- 1) Isothermal expansion @ T_1 (Heat bath)
- 2) Isochoric decompression @ $V_2 = \text{const.}$,
- 3) Isothermal compression @ T_2 (Cold sink)
- 4) Isochoric compression $V_1 = \text{const.}$,

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

Total work done by system $w = w_1 + w_2 < 0$

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

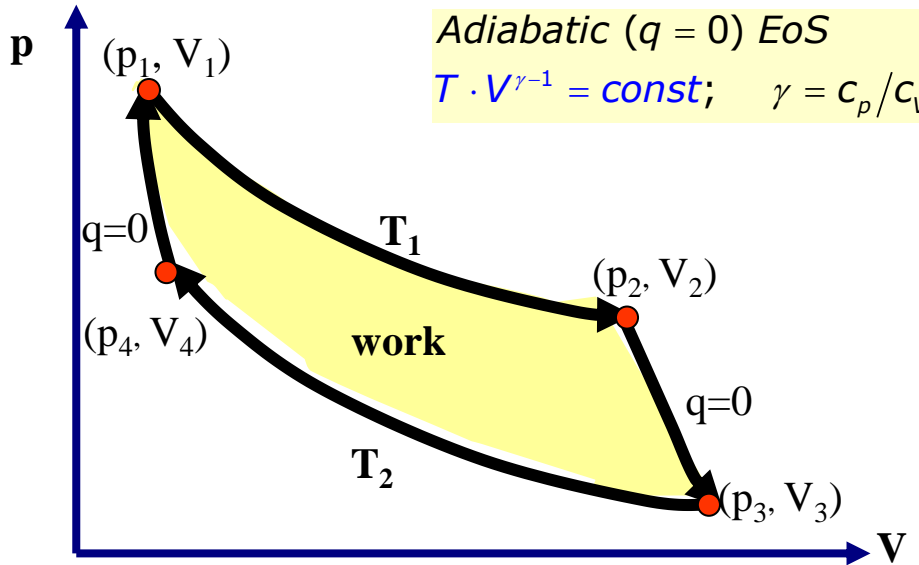
The gas absorbs heat energy and does work,

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

Not all heat is converted, some is waste heat.

Net effect: System absorbs external heat \rightarrow
 \rightarrow and does work on surroundings (=engine).

Carnot Cycle



Similar to previous examples:

1. Isothermal expansion @ $T_h = T_1$
 2. Adiabatic expansion $T_h \rightarrow T_c = T_2$
 3. Isothermal compression @ $T_c < T_h$
 4. Adiabatic compression $T_c \rightarrow T_h$
- Adiabatic works cancel: $w_{23} + w_{41} = 0$

Adiab. expansion/compr. →

$$V_4/V_1 = V_3/V_2 \rightarrow V_4/V_3 = V_1/V_2$$

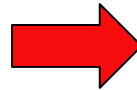
Energy balance: $w = q_1 + q_2 > 0$

on isothermal portions: $q_1/T_1 = -q_2/T_2$

Exchange with external surroundings

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

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



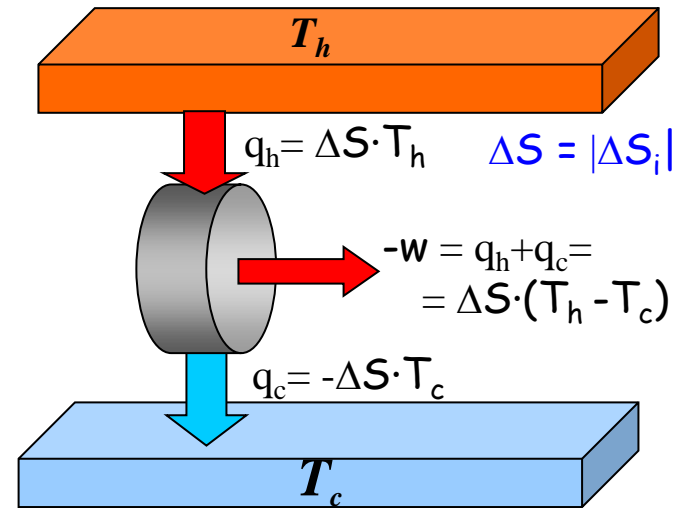
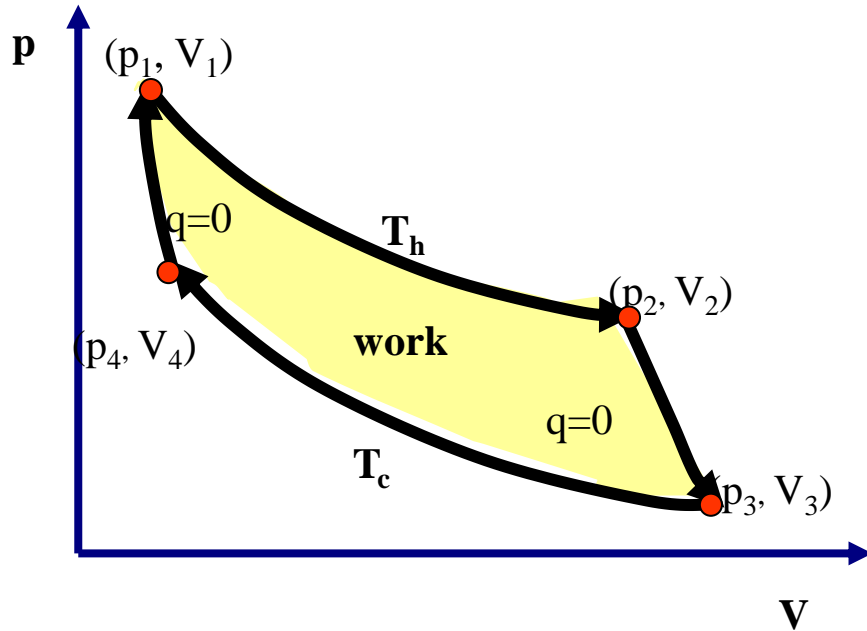
$$\Delta S_1 = \frac{q_1}{T_1} = -\frac{q_2}{T_2} = -\Delta S_2 > 0 \rightarrow \boxed{\Delta S_1 + \Delta S_2 = 0}$$

$$\boxed{|\Delta S_1| = |\Delta S_2| = \Delta S}$$

S = state function For any process: $\Delta S_{A \rightarrow B} \geq \frac{q_{A \rightarrow B}}{T} = \text{sign only for reversible } A \rightarrow B.$

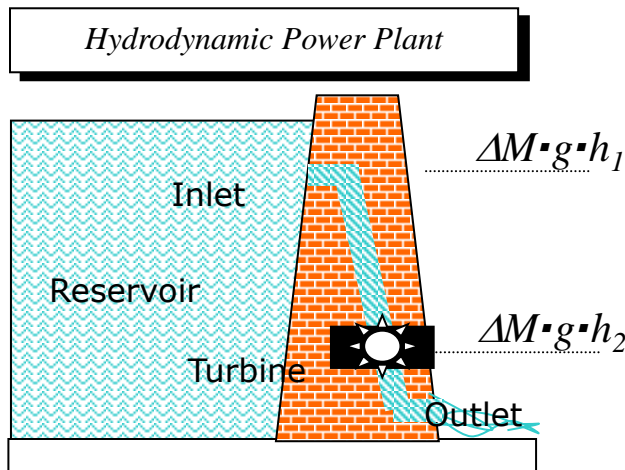
For irreversible processes $\Delta S_{A \rightarrow B} > \frac{q_{A \rightarrow B}}{T} \geq 0, \rightarrow q_{A \rightarrow B} = 0$ for intrinsic equilibration

Entropy Flow in Carnot Engines



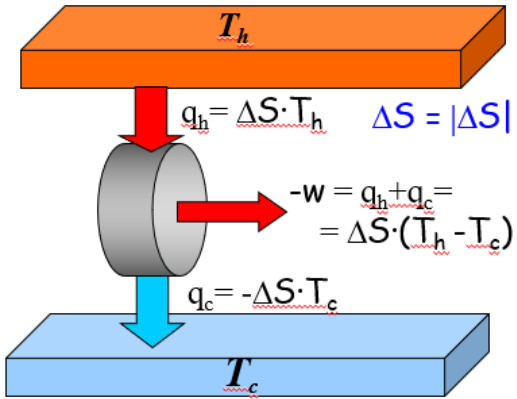
Entropy ΔS from the hot reservoir enters the engine: heat $q_h = \Delta S \cdot T_h$, **produces work** and leaves it again with a heat energy of $-q_c = \Delta S \cdot T_c$, which is dumped into cold sink.

Analogy: Reservoir water stream (ΔM), $V_1 = \Delta M \cdot g \cdot h_1 \rightarrow$ hydro-turbine, produces work, leaves with $V_2 = \Delta M \cdot g \cdot h_2$ dumped into the river. Work $w = \Delta M \cdot g \cdot (h_2 - h_1) < 0$



Mass flow $j_M \propto dM/dt$. Entropy flow $j_S \propto dS/dt$
 $j_S = F(T) j_q \sim$ heat flow

Efficiency of Carnot Engines

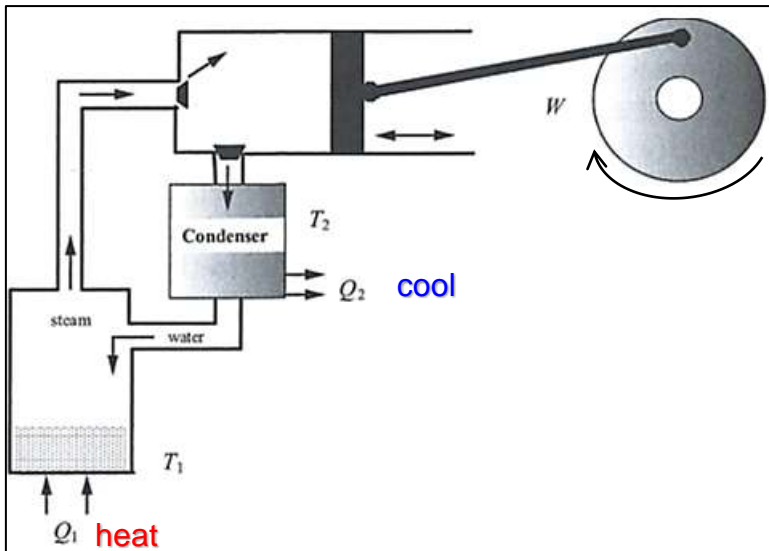


Theoretical Carnot Efficiency

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

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

Schematic of Thermal Engine



Process at $p, T = \text{const.}$

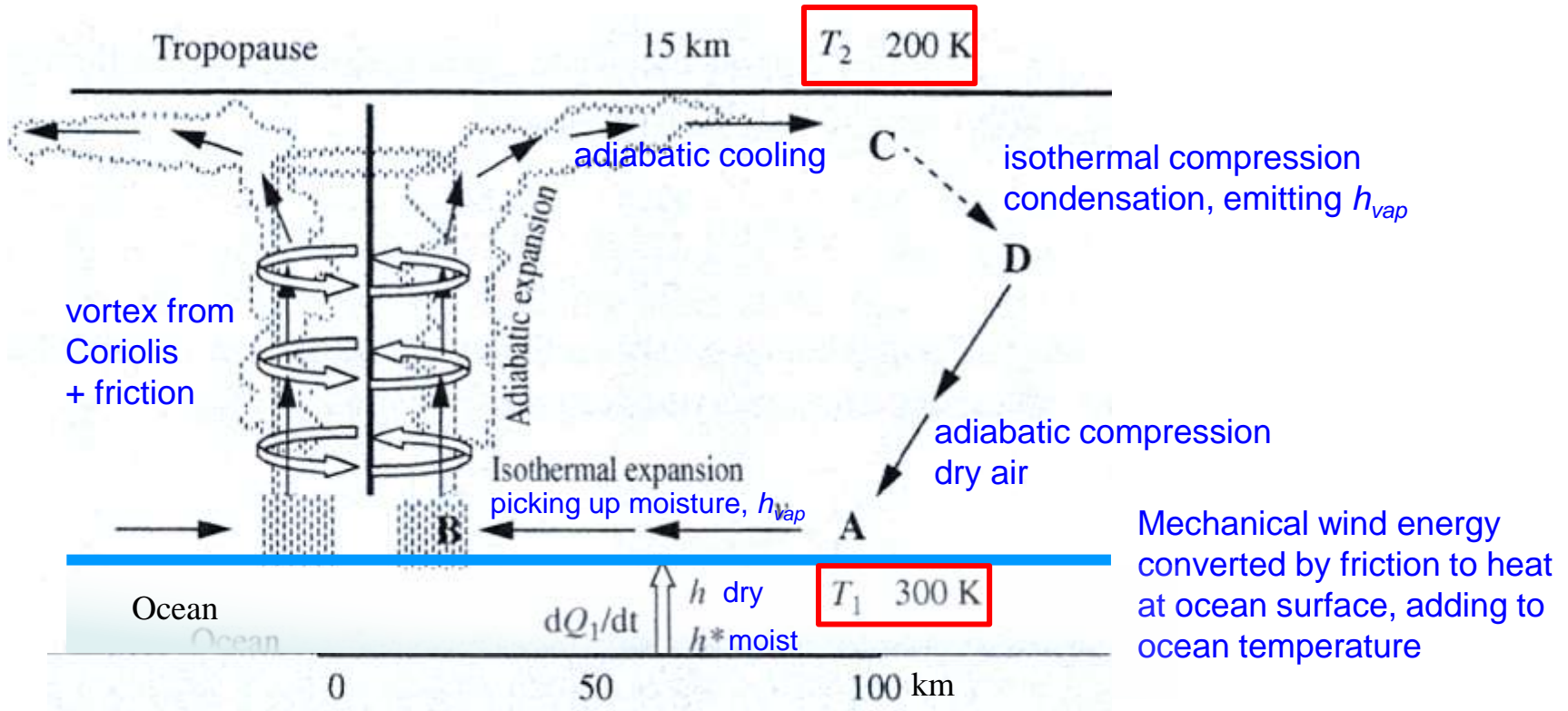
$$\xrightarrow{U = \text{const}} q = \Delta H \rightarrow$$

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

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

Cyclone Weather Pattern: Hurricane

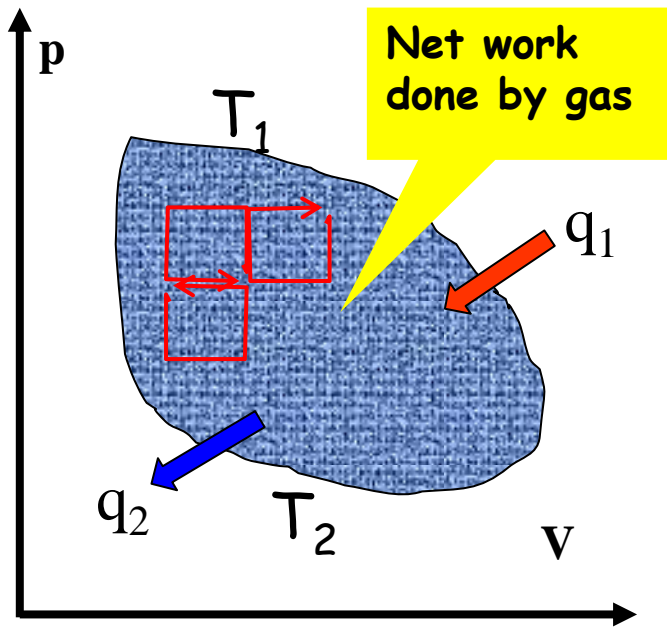
After: Kondepudi, pp. 117-120



Hurricane mechanical energy $\frac{dW}{dt} \sim \left(\frac{T_1 - T_2}{T_2} \right) \frac{dQ}{dt}$ *partially dissipated at surface*

Maximum wind speed $|v_{\max}| \sim \sqrt{\left(\frac{T_1 - T_2}{T_2} \right) (h^* - h)}$

Thermal Engines: Principle of Operation



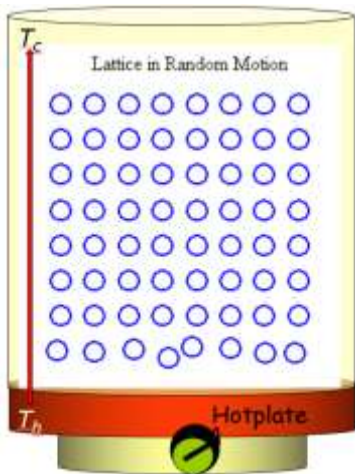
Make an arbitrary cyclic process out of elementary isothermal and isochoric processes →

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 done on surroundings by the gas.

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

Spontaneous Reactions Require Free Energy Gradient



System in contact with an external energy donor
("Heat Bath" @ $T = \text{const.}$).

Bath can provide work-equivalent heat q_{surr} at no "cost"
($T = \text{const.}$) converted into **non-trivial (non-pV)** work

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

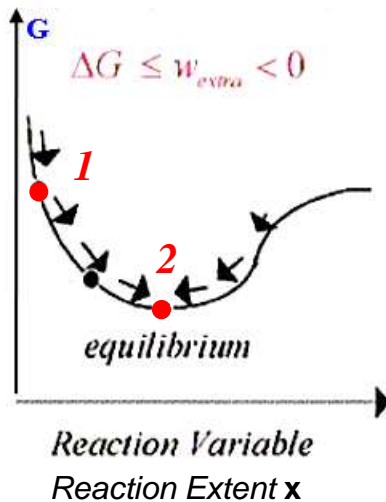
Consider isothermal reaction $1 \rightarrow 2$ at $T, p = \text{const.}$:

When is $\Delta S_{1 \rightarrow 2} > 0$ (spontaneous) and produces W_{extra} ?

Criteria for spontaneous equilibration

Eta - Theorem :

$$S < S_{\text{max}} \rightarrow dS/dt > 0$$



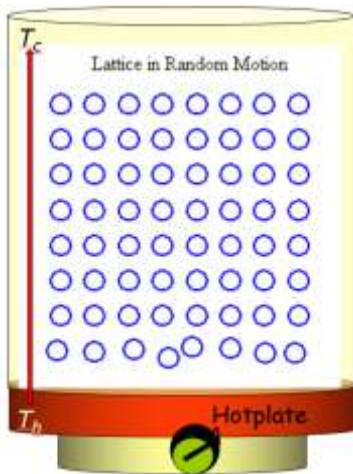
Extent $x(t)$ of reaction $\sum_k \nu_k \cdot N_k = 0$;

stoichiometric coefficients $\nu_k < 0$ for reagents N_k , products > 0

$$N_k(t) = N_k(t=0) + \nu_k \cdot x(t) \rightarrow 0 \leq x(t) \leq 1$$

$$\rightarrow \frac{d}{dt} = \left(\frac{dx}{dt} \right) \frac{d}{dx} \sim \frac{d}{dx}; \text{ rate of conversion } \nu_{\text{rxn}} = \left(\frac{dx}{dt} \right)$$

Spontaneous Reactions Require Free Energy Gradient



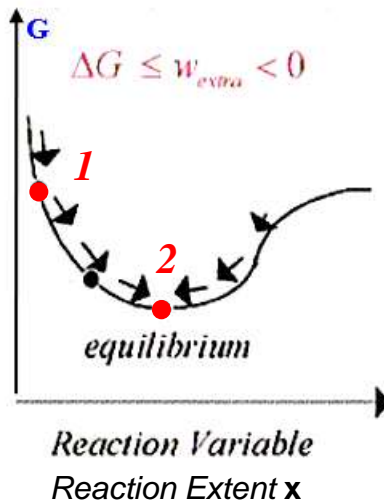
Eta - Theorem : $S < S_{\max} \rightarrow \partial S / \partial t > 0$ *spontaneous*

Spontaneous processes occur whenever

$$\frac{\partial}{\partial x} A(V, T, N) < 0 \quad \text{or} \quad \frac{\partial}{\partial x} G(p, T, N) < 0$$

Helmholtz Free energy $A(V, T, N) = U - T \cdot S$

Free energy $G(p, T, N) = (U + p \cdot V) - T \cdot S = H - T \cdot S$



$$\Delta_{1 \rightarrow 2} G < 0 \rightarrow \Delta_{1 \rightarrow 2} H < \Delta_{1 \rightarrow 2} (T \cdot S) \rightarrow$$

$$\Delta_{1 \rightarrow 2} (T \cdot S) > [H_2 - H_1] = \Delta_{1 \rightarrow 2} (U + p \cdot V)$$

$$\Delta_{1 \rightarrow 2} (T \cdot S) > (U_2 - U_1) + p \cdot (V_2 - V_1) = \Delta_{1 \rightarrow 2} U - w_{1 \rightarrow 2}$$

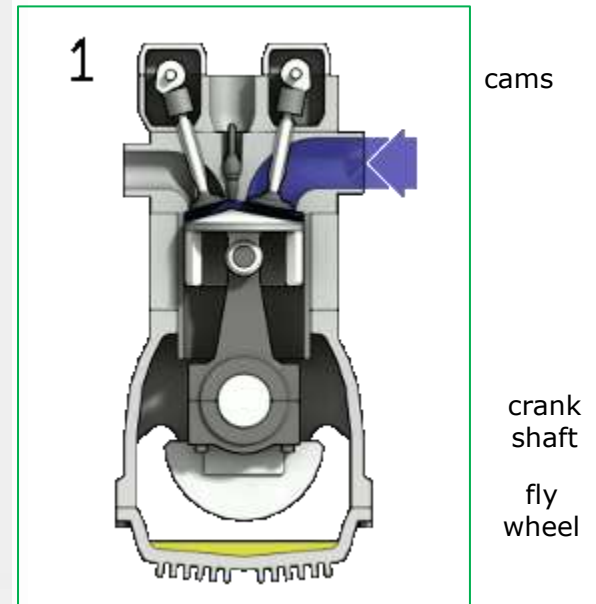
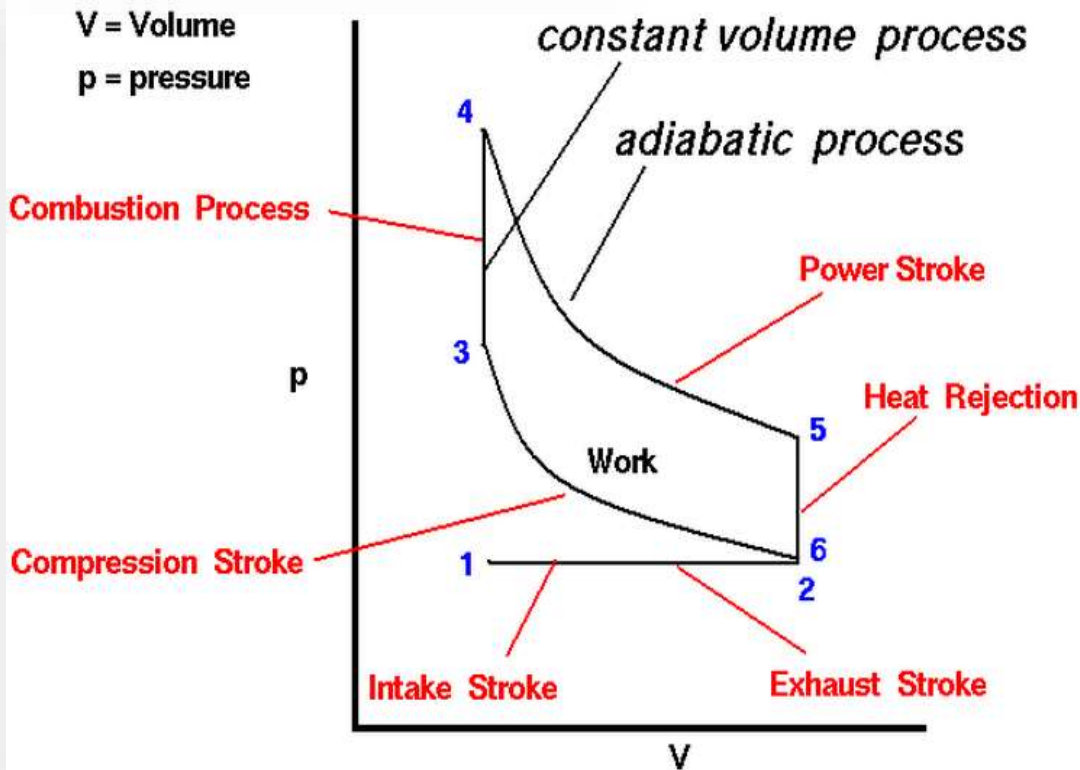
$$\Rightarrow \Delta_{1 \rightarrow 2} S > dq_{1 \rightarrow 2} / T \rightarrow \textit{spontaneous, not reversible}$$

$$\textit{Spontaneous} : \frac{dS}{dx} > \frac{1}{T} \frac{dq}{dx}$$

Ideal Otto Cycle



- 1) Intake stroke (1→2), gasoline vapor and air drawn into engine.
- 2) Compression stroke (2→3) . p, T increase.
- 3) Combustion (spark) (3→4), short time, $V = \text{constant}$. Heat absorbed from high- T "reservoir".
- 4) Power stroke: expansion (4→5).
- 5) Valve exhaust: Valve opens, gas can escape.
- 6) Emission of heat (5→6) to $low-T$ reservoir.
- 7) Exhaust stroke (6→1), piston evacuates cylinder.



Energetics of Otto Cycle

C_v = Specific Heat constant volume

γ = Specific Heat Ratio

p = pressure

T = Temperature

V = Volume

f = fuel / air ratio

Q = Fuel heating value

$c p s$ = cycles per second

P = Power

$V_2/V_3 = r$ = Compression Ratio

Compression Stroke :

$$T_3/T_2 = r^{\gamma-1}$$

$$p_3/p_2 = r^{\gamma}$$

Combustion :

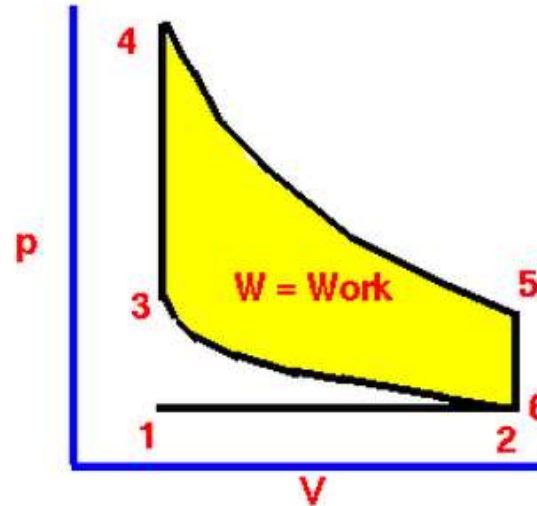
$$T_4 = T_3 + fQ/c_v$$

$$p_4 = p_3(T_4/T_3)$$

Power Stroke :

$$T_5/T_4 = r^{1-\gamma}$$

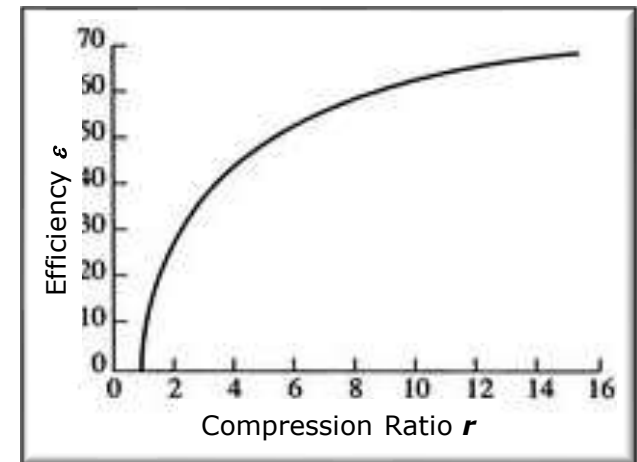
$$p_5/p_4 = r^{-\gamma}$$



$$\text{Efficiency : } \varepsilon = \frac{w}{q_{3 \rightarrow 4}} = \frac{q_{3 \rightarrow 4} + q_{5 \rightarrow 6}}{q_{3 \rightarrow 4}} = \frac{c_v(T_4 - T_3) + c_v(T_6 - T_5)}{c_v(T_4 - T_3)}$$

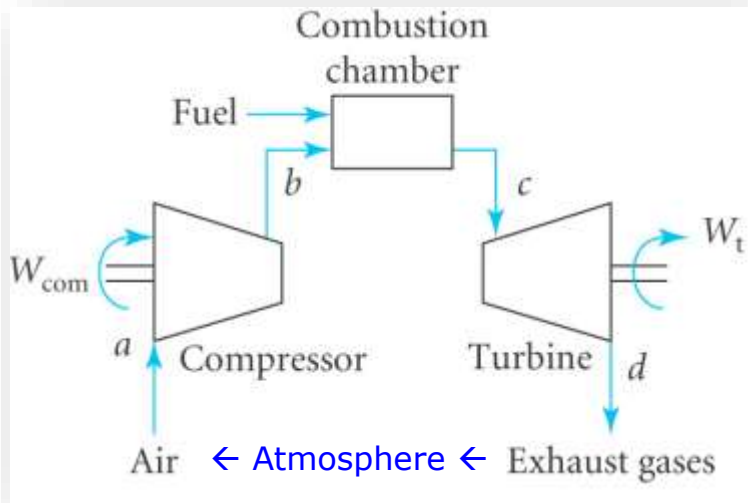
$$\varepsilon = 1 - \frac{(T_5 - T_6)}{(T_4 - T_3)}$$

$$\text{Adiabatic EoS } [T \cdot V^{R/c_v} = \text{const.}] \rightarrow \boxed{\varepsilon = 1 - r^{-R/c_v}}$$



Brayton/Joule Turbine Cycle

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Open cycle (aircraft power plant):

- a-b Compression ($\times 10-20$), adiabatic $q=0$
- b-c Combustion ($p=const.$)
- c-d Turbine work, $w_t \neq 0$, adiabatic ($q=0$)
- d-a Exhaust waste energy ($p=const.$)

$$q_{b \rightarrow c} = h_c - h_b = c_p \cdot (T_c - T_b) > 0 \text{ absorbed @ } p = const$$

$$q_{d \rightarrow a} = h_a - h_d = c_p \cdot (T_a - T_d) < 0 \text{ emitted @ } p = const$$

$$w_{com} = h_b - h_a = c_p \cdot (T_b - T_a) > 0 \text{ received @ } q = 0$$

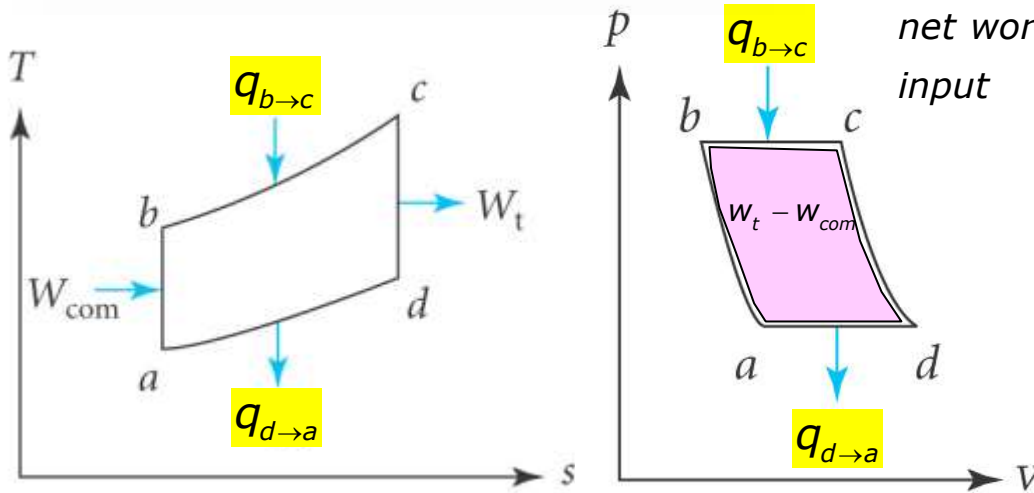
$$w_t = h_c - h_d = c_p \cdot (T_c - T_d) < 0 \text{ done @ } q = 0$$

$$\text{net work } w = w_t - w_{com} = (h_c - h_d) - (h_b - h_a)$$

$$\text{input } q_{b \rightarrow c} = h_c - h_b$$

$$\varepsilon = \frac{w}{q_{b \rightarrow c}} = \frac{(h_c - h_d) - (h_b - h_a)}{h_c - h_b}$$

$$\varepsilon = 1 - \frac{h_d - h_a}{h_c - h_b}$$



$$\text{Adiabatic EOS: } \varepsilon = 1 - \left(\frac{p_b}{p_a} \right)^{\frac{c_v - 1}{c_p}}$$

$$\text{Compression } p_b/p_a=10, c_p/c_v=1.3 \rightarrow \varepsilon=0.41$$

Turbine exhaust still very hot \rightarrow can use again

End of IG Applications