Agenda

Energy conservation, conversion, and transformation

- Potential energy, kinetic energy, work, and power
  - Variable force, chemical rearrangement energy (Enthalpy)
  - Examples

- Kinetic energy transfer,
  - Dissipation, randomization and spontaneous processes
  - Examples of thermal motion, Maxwell-Boltzmann distribution

- Transfer of thermal energy (heat)
  - Conduction, convection, radiation (cooling)
  - Internal energy, equivalence of work and heat
  - Basic (First Law & Second) Laws of Thermodynamics,
  - Entropy and spontaneous processes.

- Thermal engines
  - Ideal Carnot processes
  - Real gases/substances

- Electricity and Electromagnetic Power

Basic Laws of Statistical Thermodynamics

Consider complex systems: Many degrees of freedom (=many particles, particles with complex structure, complex internal energy states, complex materials with different phases,.., chaos)

Observation of dissipative phenomena: Excitation of complex systems initiates evolution toward maximum dissipation (Equilibrium)

Statistical Thermodynamics: Physics of equilibration & equilibrium

0) Systems in contact equalize mean internal (kinetic) energies,
→ temperatures equalize.
"Canonical & grand canonical" ensembles (of many ident. systems).

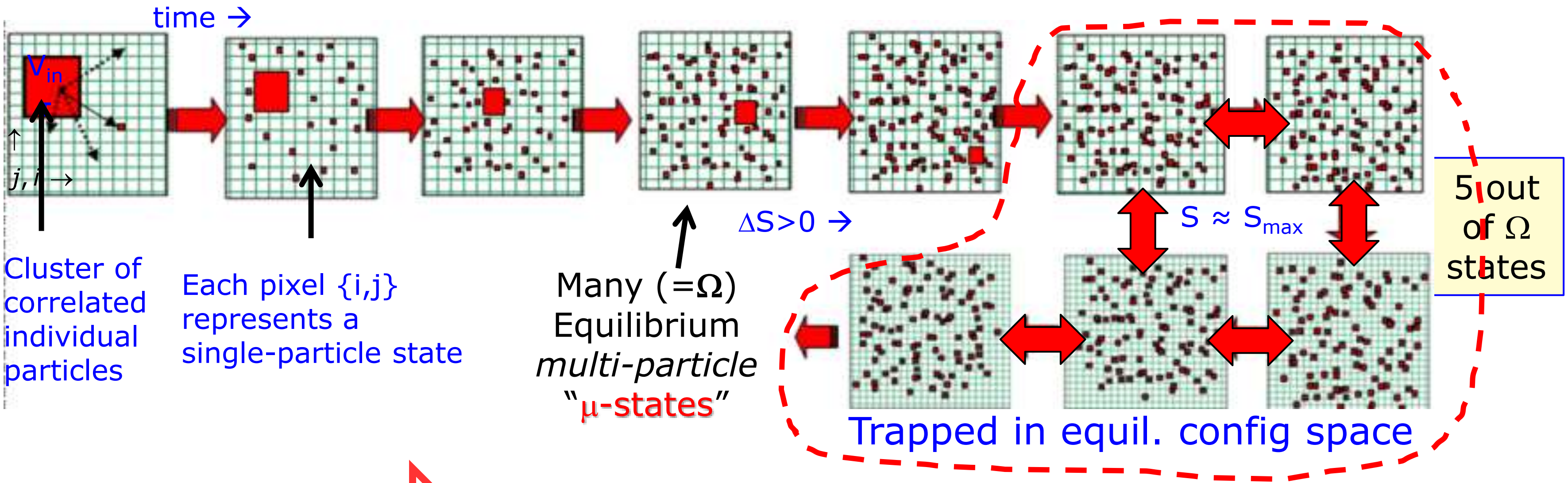
1) Energy (of system plus surroundings) is conserved.

2) Complex systems evolve spontaneously toward state of maximum randomness (complexity)→ Measure=Entropy.

3) There exists an absolute "zero point" of energy for any system: energy and complexity are at a minimum (@ absolute *T=0 K*).

Randomization: Spontaneous Dissolution of Cluster

Transitions from one *s.p.* state (pixel$_i$) to another (pixel$_j$) are micro-reversible (unlikely).



Cluster of correlated individual particles

Each pixel {i,j} represents a single-particle state

Many (=Ω) Equilibrium *multi-particle* "μ-states"

5 out of Ω states

Trapped in equil. config space

Naturally spontaneous

Natural direction of spontaneous process: Number Ω of visited multi-particle μstates increases in time, <u>from simple to complex</u>. ➔ Essentially irreversible.

$1 \ll \Omega = \#\ visited\ \ m.p.\ states\,(configs).\ Example\ in\ 2D \rightarrow \Omega \sim 10^{200} \rightarrow use\ Ln\,\Omega$

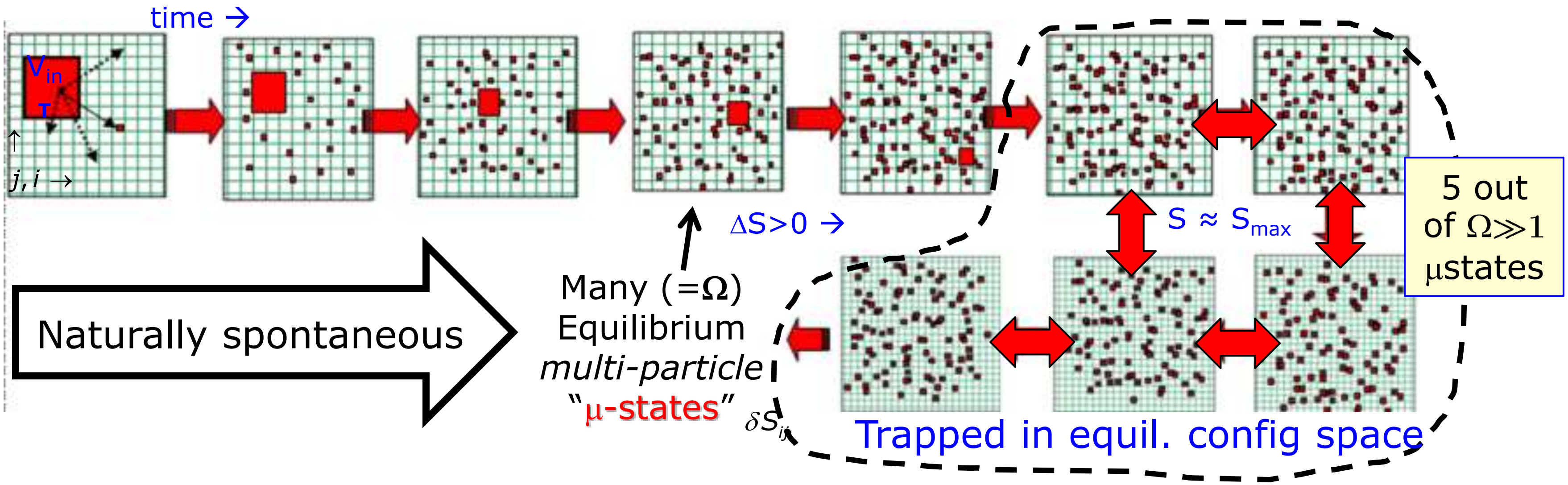
$Maximize\ mean\ occupation\ of\ \ s.p.\ state\{i,j\}/\mu - state\ \&\,\Omega = \#of\ m.p.\,\mu - states$

$"Entropy"$ $\boxed{S := k_B \cdot Ln\,\Omega = -k_B \cdot \sum_{i,j} p_{ij}\,Ln\,p_{ij}}$ $p_{ij} \sim 1/\Omega$ $\boxed{\Omega(S) = e^{S/k_B}}$

S= State Function; Boltzmann (1877)

Randomization: Spontaneous Dissolution of Cluster

Transitions from one *s.p.* state (pixel_i) to another (pixel_j) are micro-reversible (unlikely).



Naturally spontaneous

Many (=Ω)
Equilibrium
multi-particle
"μ-states"

5 out of Ω≫1 μstates

Trapped in equil. config space

$$\text{"}\mathit{Entropy}\text{"} \quad \boxed{S := k_B \cdot Ln\ \Omega = -k_B \cdot \sum\nolimits_{i,j} p_{ij} \cdot Ln\, p_{ij}}$$

Occupation probability of s.p. state $\{i, j\}$

in any given μstate : $p_{ij} \sim 1/\Omega$

$$p_{ij} = \begin{cases} 0 & \text{if nowhere} \\ 1/\Omega & \text{if everywhere} \end{cases}$$

Quantitative Measure (microscopic)

$$\boxed{\begin{array}{l} \mathit{Order}: p_{ij} = \{0,1\} \rightarrow \delta S_{ij} = 0 \\ \mathit{Random}: \{0,1\} \neq p_{ij} \cong 1/\Omega \rightarrow \delta S_{ij} > 0 \end{array}}$$

$$\boxed{\Omega(S) = e^{S/k_B}}$$

2. *Law of TD: Entropy increases in spontaneous processes* $\Delta S/\Delta t > 0$

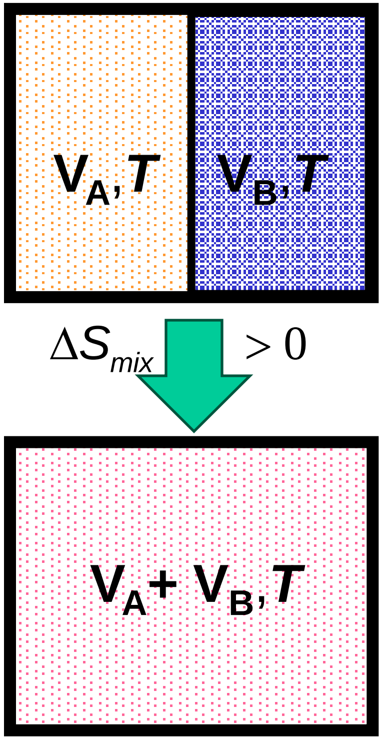
Entropy of Mixing: Example

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 $\varpi_B \propto V_B$

No change in energy
$\Delta q = 0$

When partition is removed, the gases will mix.



Information on s.p. configuration space from EoS

Ideal gases $P \cdot V = n \cdot R \cdot T \rightarrow \varpi_{A,B} \propto V_{A,B} \propto n_{A,B}$

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"

$$\Delta S_{mix} = -nR\left\{\frac{n_A}{n}\cdot Ln\left(\frac{n_A}{n}\right) + \frac{n_B}{n}\cdot Ln\left(\frac{n_B}{n}\right)\right\} =$$

$$= -2R\left\{0.5\cdot Ln(0.5) + 0.5\cdot Ln(0.5)\right\} = 11.5J/mol\cdot K > 0$$

Entropy is gained ←→ mixing occurs spontaneously.

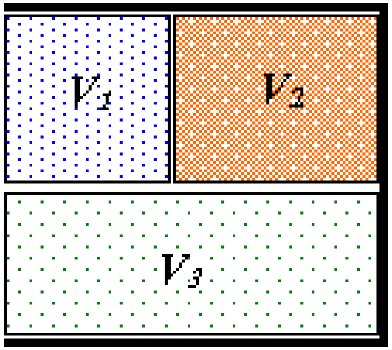
$$\Delta S \geq \frac{\Delta q}{T} \text{ in spontaneous processes}$$

Mixed gases are difficult to unmix (costs energy)!

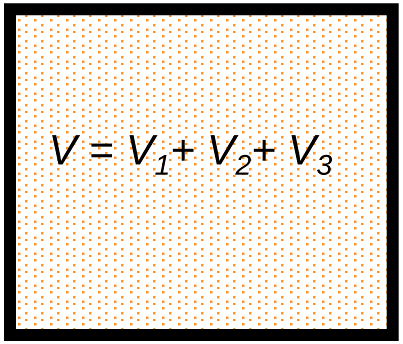
Universal Gas Constant
R=8.31*J/mol·K*

EoS: Entropy of Mixing

Separated Gases



Mixed Gases



S - gain by individual gas components

$$\Delta S_i = n_i \cdot R \cdot Ln\left(\frac{V}{V_i}\right) > 0 \qquad n_i = number\ \ of\ \ moles\ i$$

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

$$\Rightarrow \quad \Delta S = -R \cdot \sum_i n_i \cdot Ln\left(\frac{V_i}{V}\right) > 0 \qquad S \nearrow$$

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

Relative abundance (*probability for*) *particle type i*

$$p_i = \frac{n_i}{n} = \frac{V_i}{V} < 1 \qquad \boxed{\Delta S = -n \cdot R \cdot \sum_i p_i \cdot Ln\, p_i}\ \ n\ \ moles$$

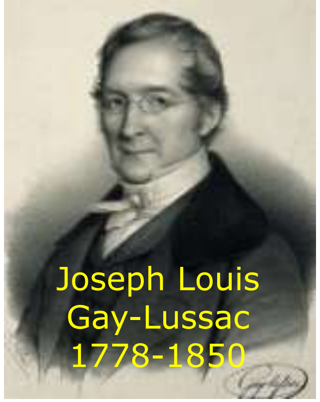
$$N\ particles\ \ \boxed{\Delta S = -N \cdot k_B \cdot \sum_i p_i \cdot Ln\, p_i}$$

Can use other "State Functions" to calculate entropy, all related by EoS

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,..

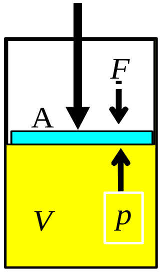
Response of dilute gases of specified amounts (#moles = *n, Avogadro*)

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 $V(T_C)=V(0^0C)\cdot\left[1+\alpha\cdot T_C\right]\rightarrow\boxed{V(T)\propto T}$ *(Kelvin)*

Compression



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

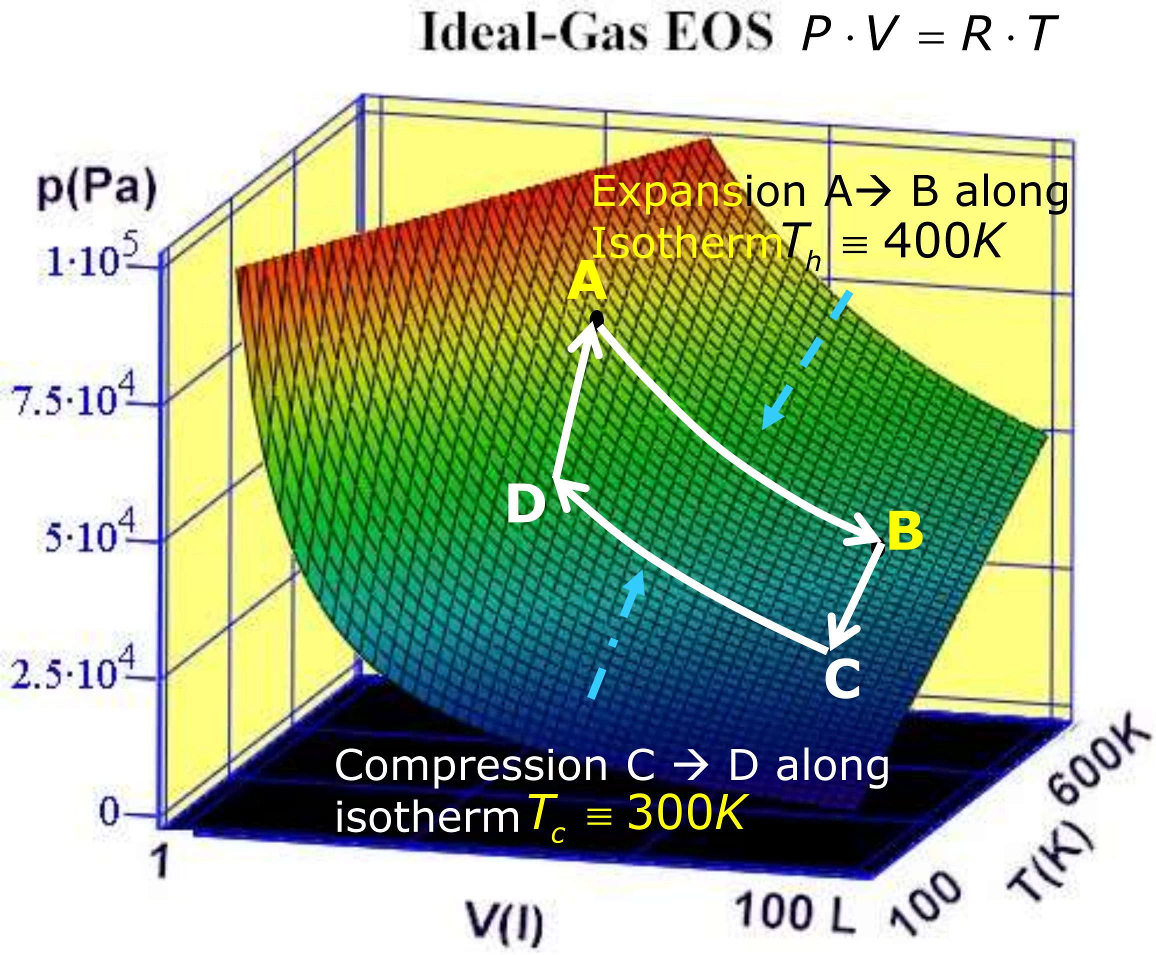
Polytrope coefficient $\gamma=C_P/C_V$

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

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

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

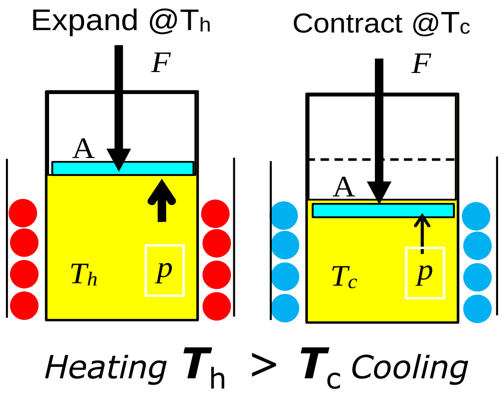
Reversible Circular Processes on EoS Hyperplane



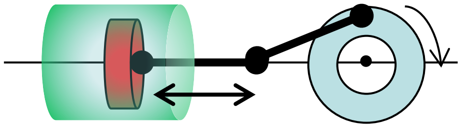
Expansion A→ B along Isotherm $T_h \equiv 400K$

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

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



Heating $T_h > T_c$ *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

Entropy and Energy at Equilibrium: Ideal Gases

Many systems in mutual contact, provide heat energy E just to System#1 $(E = E - total)$

$\rightarrow$ *eventual stationary state – maximum probability – all acquire same temperature T*

$$\left(\frac{1}{\Omega}\frac{d\Omega(E)}{dE}\right)_1 = \left(\frac{1}{\Omega}\frac{d\Omega(E)}{dE}\right)_2 = \left(\frac{1}{\Omega}\frac{d\Omega(E)}{dE}\right)_3 \cdots \Rightarrow \frac{d\Omega(E)}{\Omega dE} = \frac{d\ln[\Omega(E)]}{dE} = \underline{\underline{Const}}(E)$$

Independent of material, size, shape, amount → Function Const depends on total energy E supplied to one of the systems as heat. Dimension [Const(E)]= 1/energy.
Obvious & simplest *intensive energy* variable = temperature ***T***

→System energy content of an ideal gas (*N* particles): $P\cdot V = N\cdot k_B\cdot T$

Adopt ***intensive*** energy variable → Energy per particle

$$\boxed{\frac{E}{N}\propto\frac{P\cdot V}{N} = k_B\cdot T}$$

$$\boxed{Adopt\ intensive\ function\ S\ with\ \frac{dS}{dE} = \frac{1}{\Omega}\frac{d\Omega(E)}{dE} = \frac{d}{dE}k_B Ln\Omega(E) \propto \frac{1}{T}}$$

Simplest form compatible
S extensive

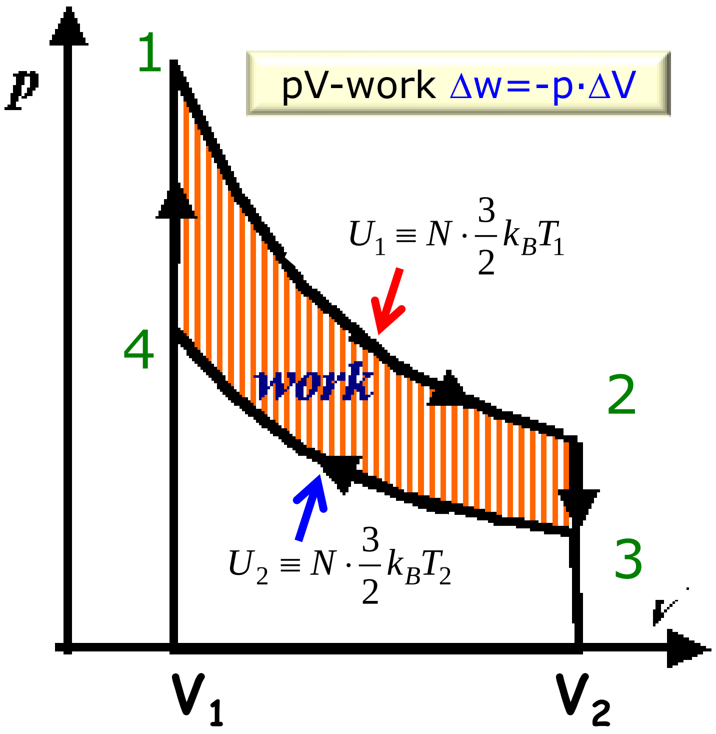
$$S(E) = k_B Ln\Omega = \cancel{S_0} + \frac{E}{T} \rightarrow Distributed\ heat\ energy\ \boxed{E = T\cdot S}$$

integration constant =0

Heat absorption / emission by system @ equil T : $\Delta\langle E\rangle = \Delta q \rightarrow \Delta S = \frac{\Delta q}{T}$

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



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

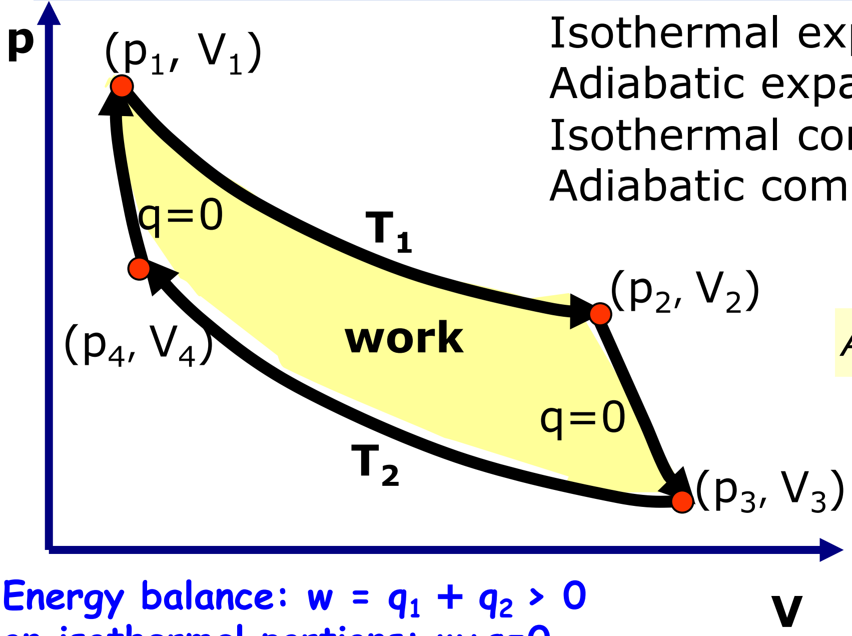
Total work by engine : $\boldsymbol{w = w_1+ w_2 < 0}$

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.

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

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

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

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

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

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

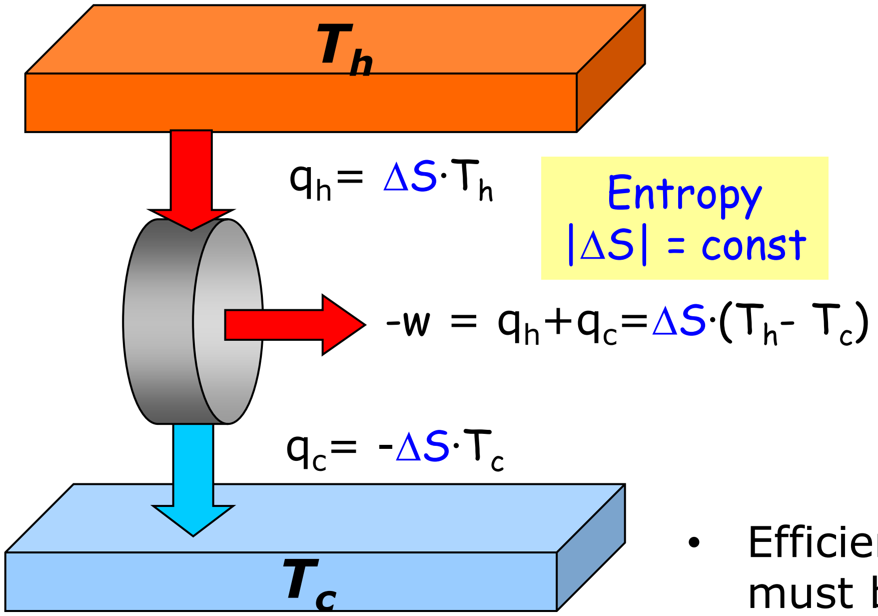
Entropy is conserved in reversible cyclic processes: $\Delta S_1 + \Delta S_2 = 0.$

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

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

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

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

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

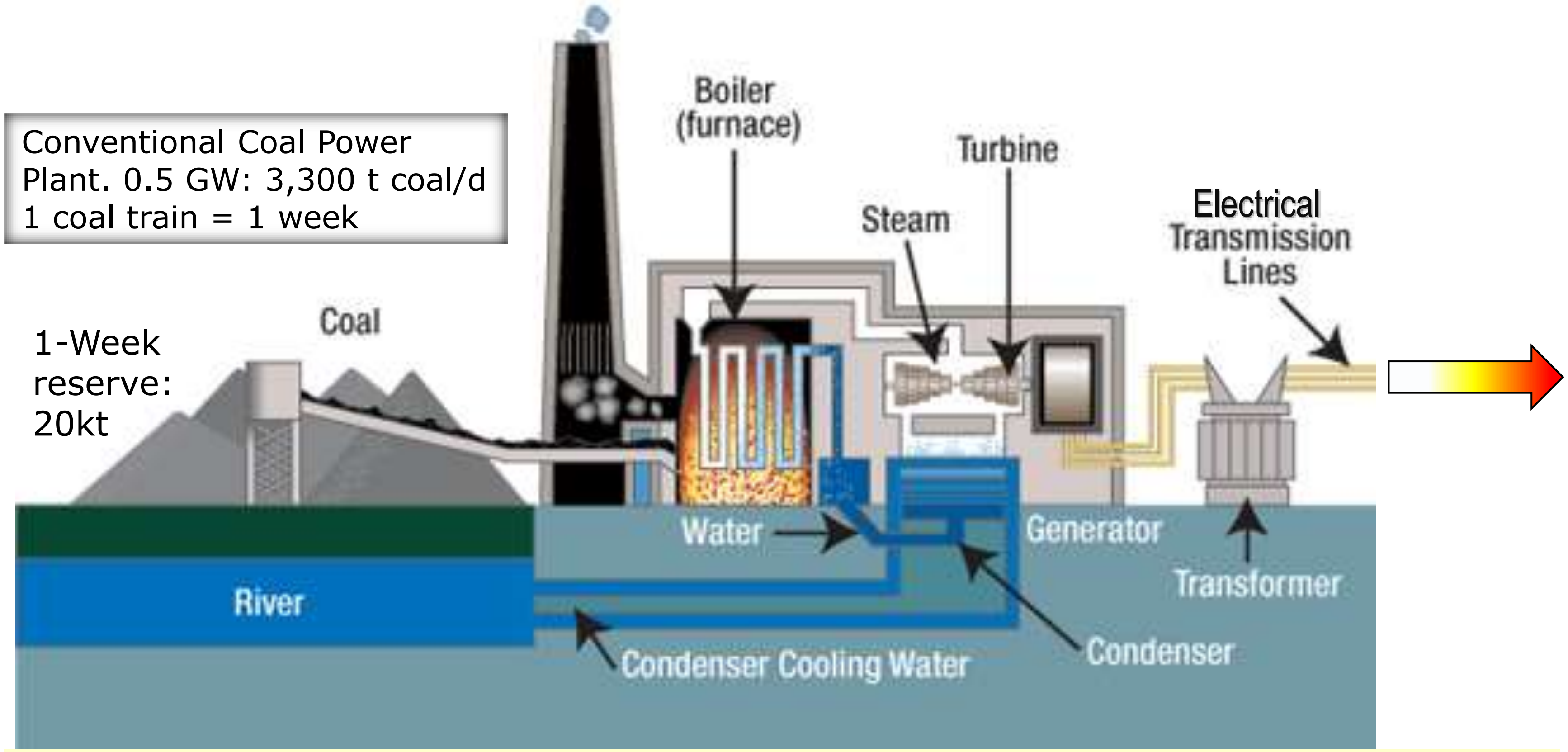
$$\varepsilon_C = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \xrightarrow[T_h \to \infty]{} 1$$

- 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 $\boxed{\varepsilon_{therm} \sim 0.3}$.

Thermal (Coal) Power Plant

Fuel → Combustion Heat → Steam → Expansion Work → Electromagnetic Work → Electrical Power



Conventional Coal Power Plant. 0.5 GW: 3,300 t coal/d
1 coal train = 1 week

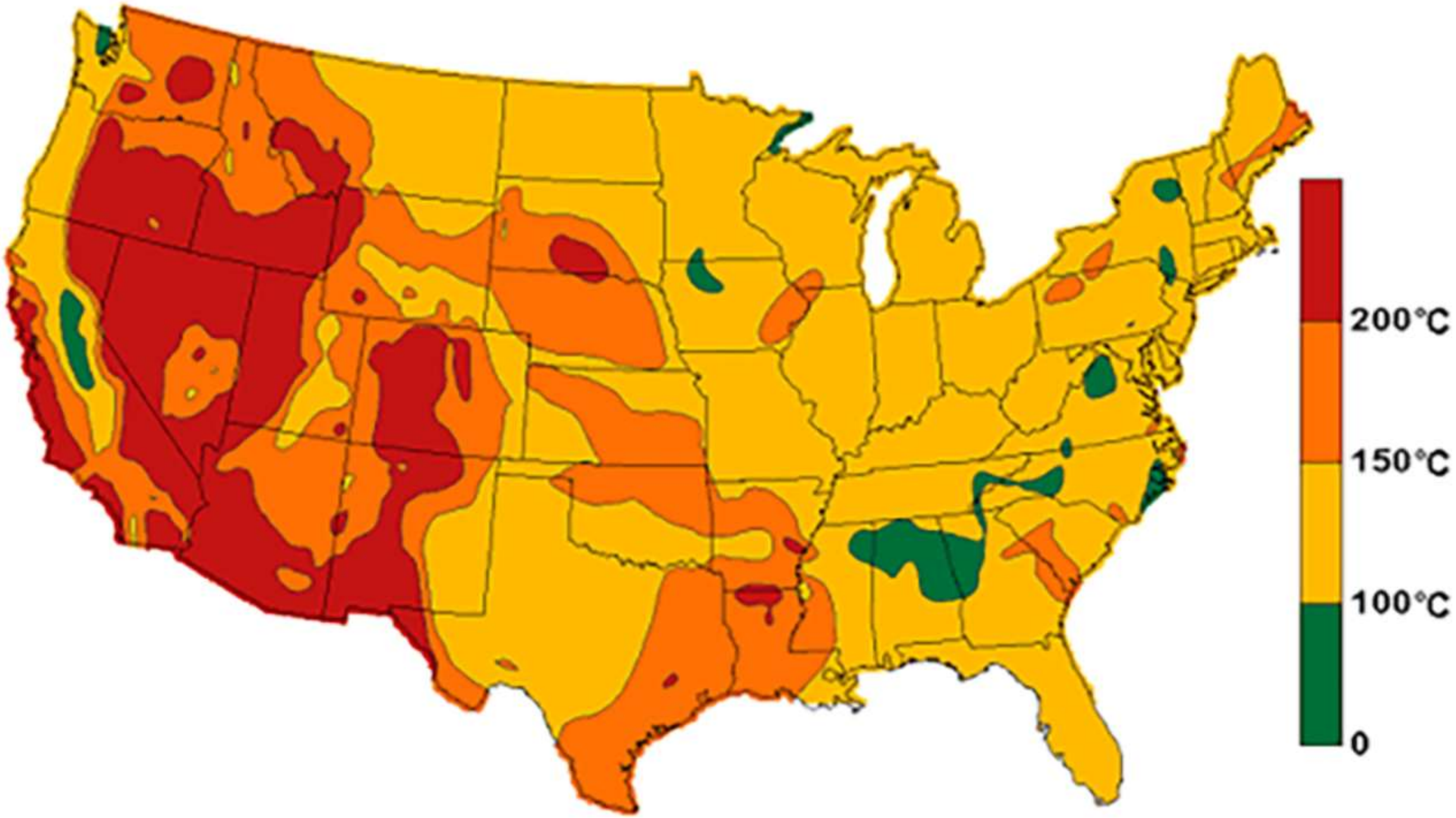
1-Week reserve: 20kt

U.S. now: 600 *large* coal-fueled electrical power plants (0.5-1GW), many (~10^3) smaller units. Predictions (BAU) by 2030: +150 (?) (≈100 GW), 12 now under construction. Newer units: combined cycle (IGCC), power/heat co-generation. → convert to nG ?

End of
Work, Energy, & Power II

Geothermal Power

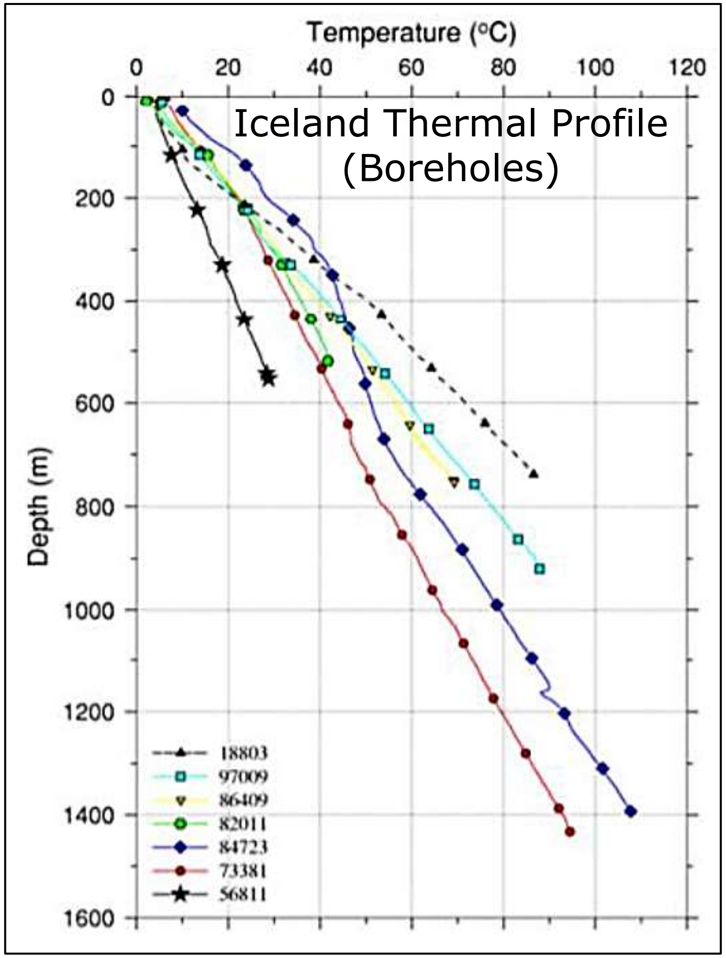
U.S. Geothermal Resources



Most of the geothermal power plants in the United States are in western states and Hawaii, where geothermal energy resources are close to the earth's surface. California generates the most electricity from geothermal energy. The Geysers dry steam reservoir in Northern California is the largest known dry steam field in the world and has been producing electricity since 1960.

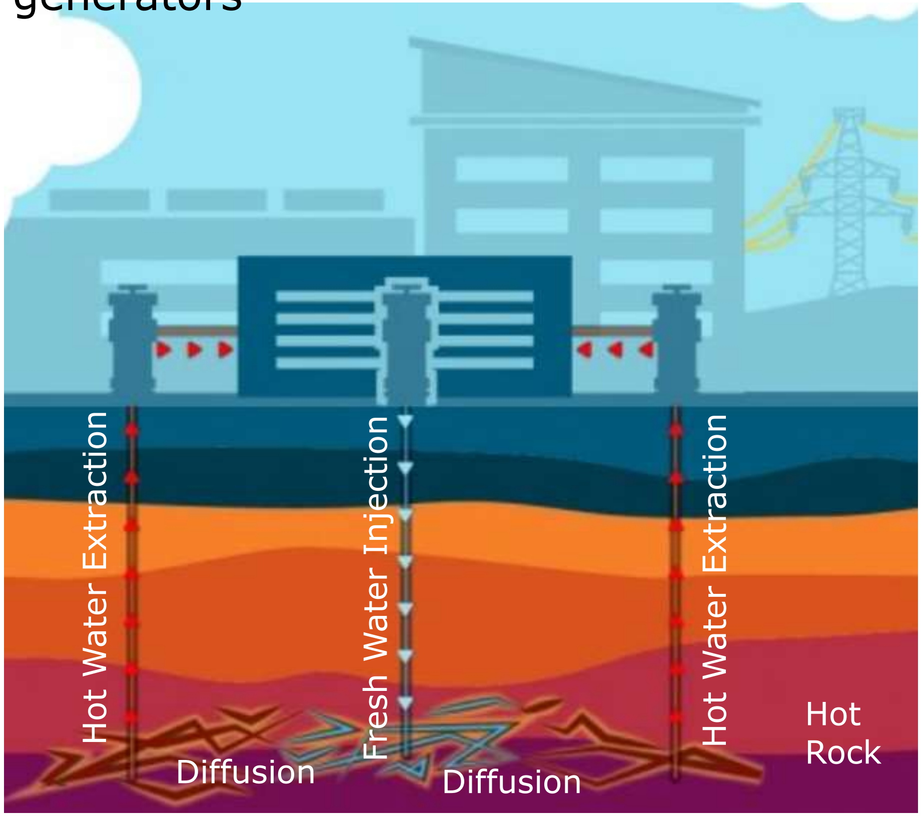
Geothermal Depth Profile

Worldwide simplest (conventional/ancient) direct use: building/district heating.
Utility: Geothermal electrical power plants, Residential: geothermal heat pumps, A/C



From H. Kennedy, 2020; citing Augustsson & Flovenz, 2--4

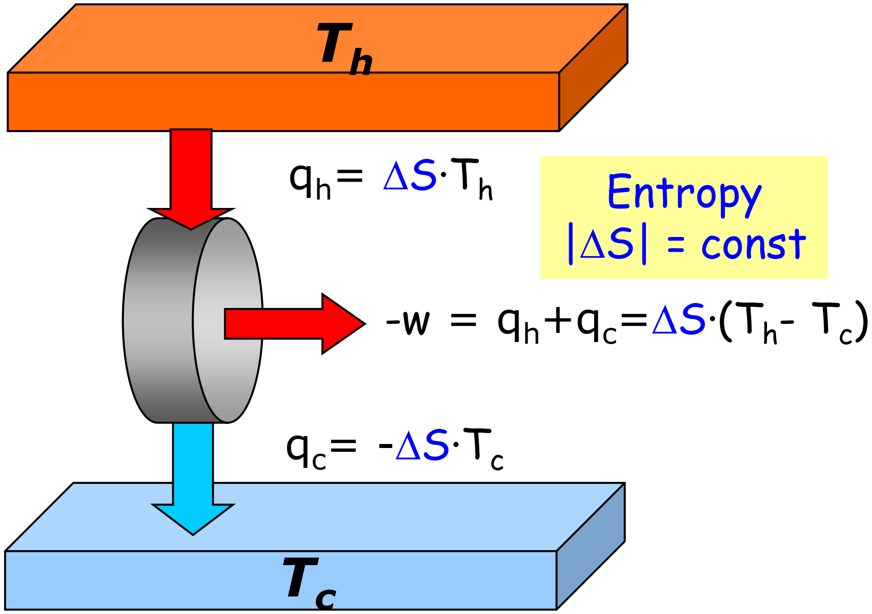
Generating technology: Inject fresh water (hydro fracturing), extract hot water → steam → drive steam turbines & electric generators



Extract Geothermal Heat: Carnot Engines

Cyclic Carnot process ***at constant entropy*** ΔS → work $\boldsymbol{w = -(q_h + q_c) < 0}$ on environment powered by transferring heat from hot to cold sink $(T_h \rightarrow T_c)$.
→ Refrigerator

Ideal Gas: Every cyclic pV engine can be modeled as Carnot process.



$q_h = \Delta S \cdot T_h$

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

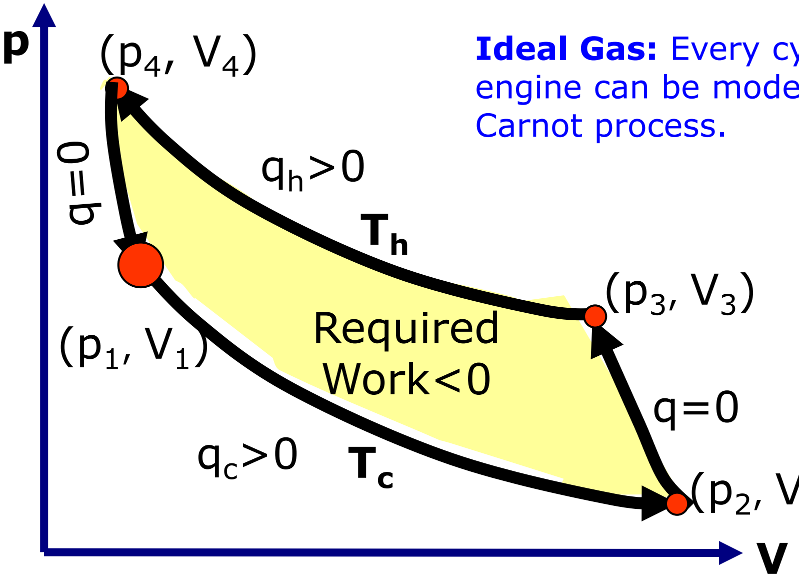
$$\boxed{\varepsilon_C = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h}}$$

- ε_C is maximum efficiency of a realistic Carnot-type engine.
- 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.

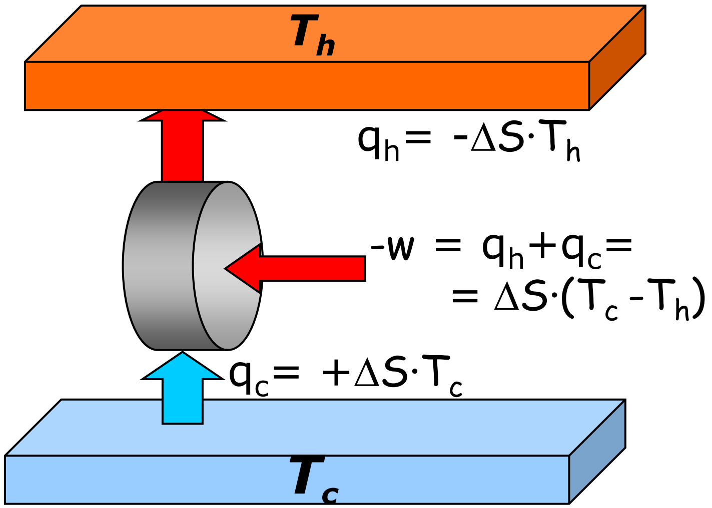
Reversing Carnot process implies sign changes of heat energies and work
→ External work $\boldsymbol{w>0}$ done on system can transfer heat from a cold reservoir to a hot reservoir $(T_c \rightarrow T_h)$.

Thermal engine efficiencies $\varepsilon_{therm} \sim 0.3$.

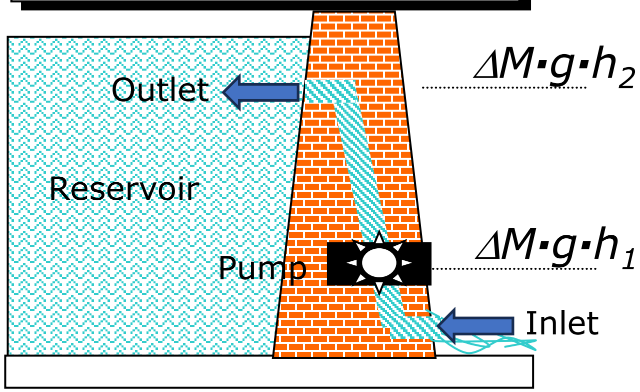
Entropy and Heat Flow in Reverse Carnot Process



Ideal Gas: Every cyclic pV engine can be modeled as Carnot process.



Pumped Energy Storage

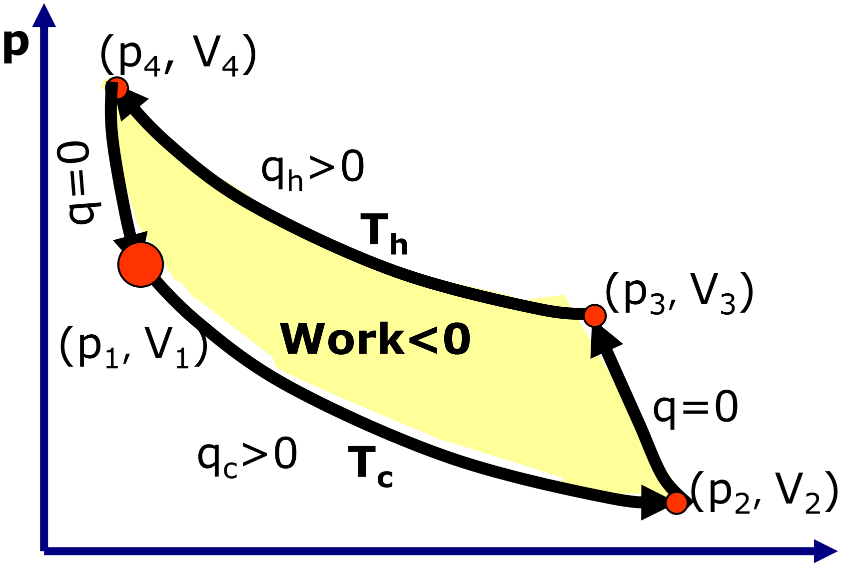


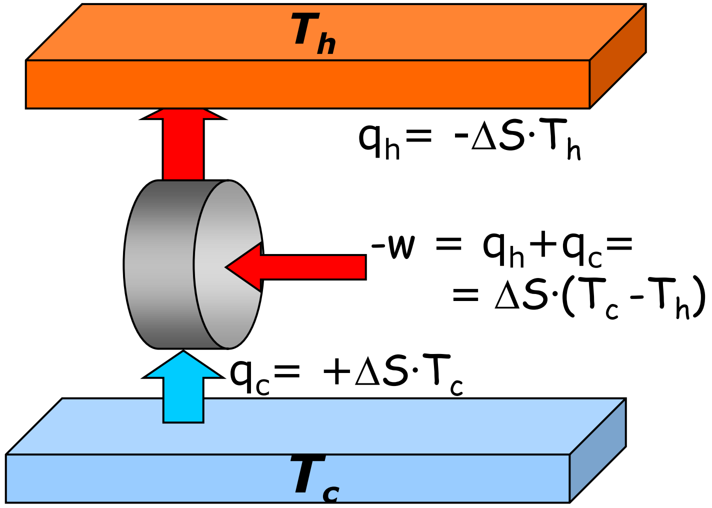
$$\text{Maximum efficiency } \boxed{\eta_C = 1 - \varepsilon_C = \frac{q_c}{q_h} = \frac{T_c}{T_h}}$$

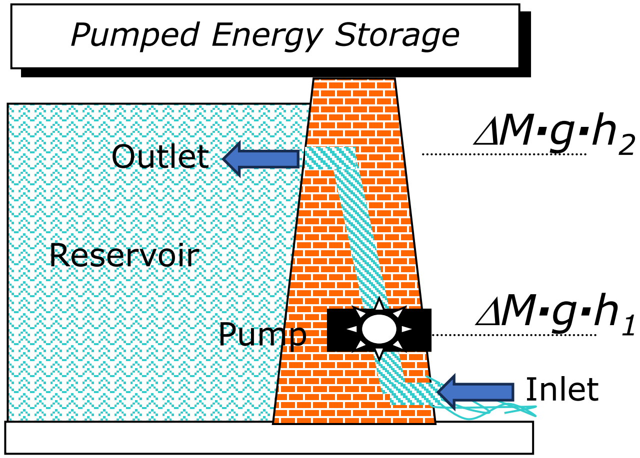
Entropy **ΔS** with heat **$q_c = \Delta S \cdot T_c$** from the **T_c** reservoir preheats the colder (**T_h**) working fluid/gas, which enters an externally powered compressor. The compressor **does work** on the fluid, raising its temperature to **T_h**. Heat energy **$\Delta S \cdot T_h$** is then transferred to the **T_h** heat reservoir.

Analog: Stream of water ΔM from a river carries energy $\Delta M \cdot g \cdot h_1$, enters an externally powered pump that lifts ΔM by $(h_2 - h_1)$ to the reservoir head at energy $\Delta M \cdot g \cdot h_2 > \Delta M \cdot g \cdot h_1$.

Entropy and Heat Flow in Reverse Carnot Process



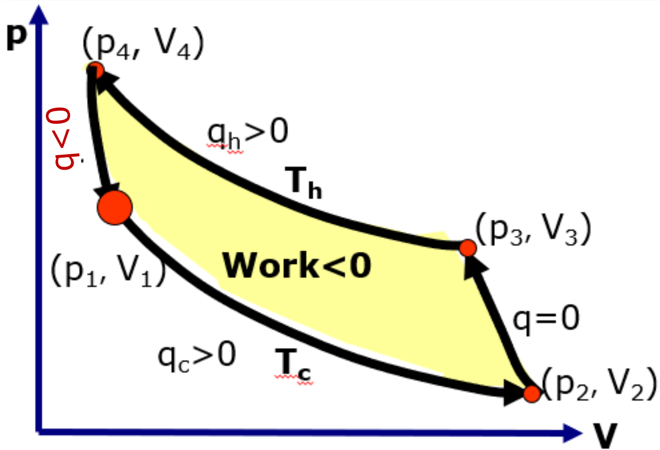




Entropy **ΔS** with a heat energy of **$\Delta S \cdot T_c$** from the **T_c** reservoir warms the colder working fluid, which enters an externally powered compressor. The compressor **does work** on the fluid, raising its temperature to **T_h**. The heat energy of **$\Delta S \cdot T_h$** can then be transferred to the heat reservoir.

Analog: Stream of water ΔM from a river carries energy $\Delta M \cdot g \cdot h_1$, enters an externally powered pump that lifts ΔM by $(h_2 - h_1)$ to the reservoir head at energy $\Delta M \cdot g \cdot h_2 > \Delta M \cdot g \cdot h_1$.

Residential Heat Pump

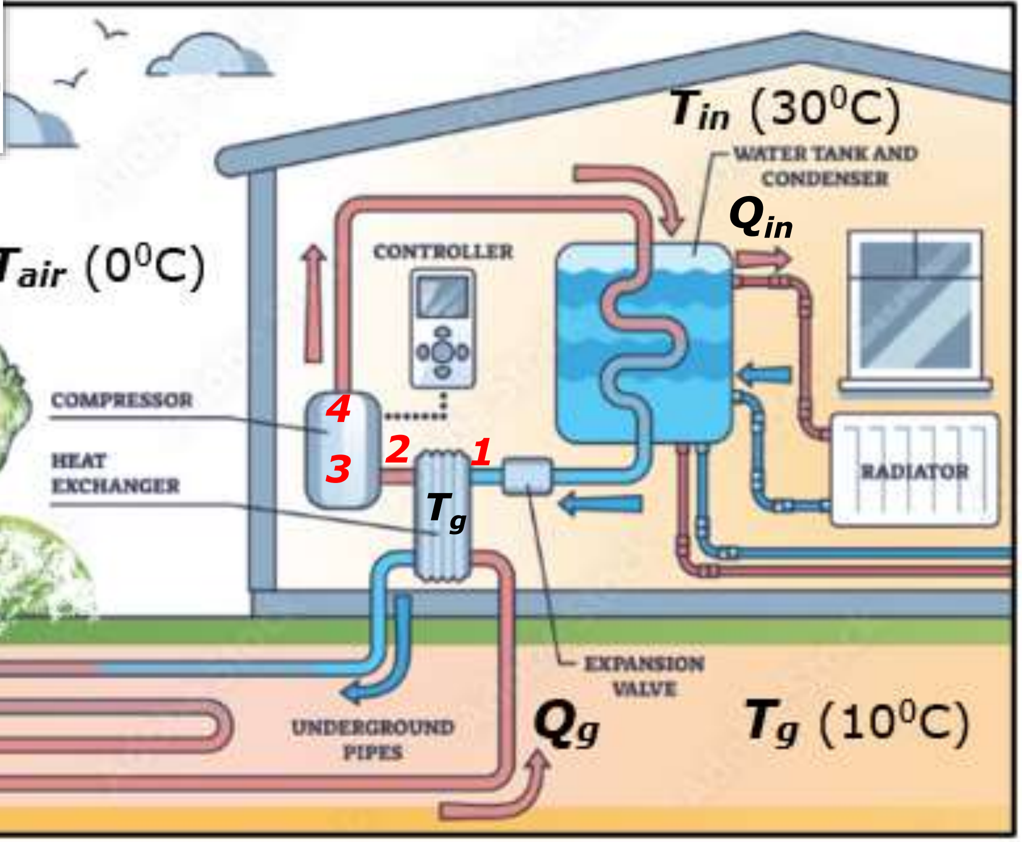


Carnot heating: In-ground heat pump absorbs heat energy $Q_g \approx \Delta S\cdot T_g$ from under ground T_g heat bath to preheat expanded work fluid/gas. Compressor provides differential heat $Q_{in} \approx -\Delta S\cdot T_{in}$ required for sustaining temperature T_{in}.

Work fluid transfers heat $Q_{in} < 0$ to tank and interior. Iso-thermal expansion after expansion nozzle in ground loop heat exchanger.

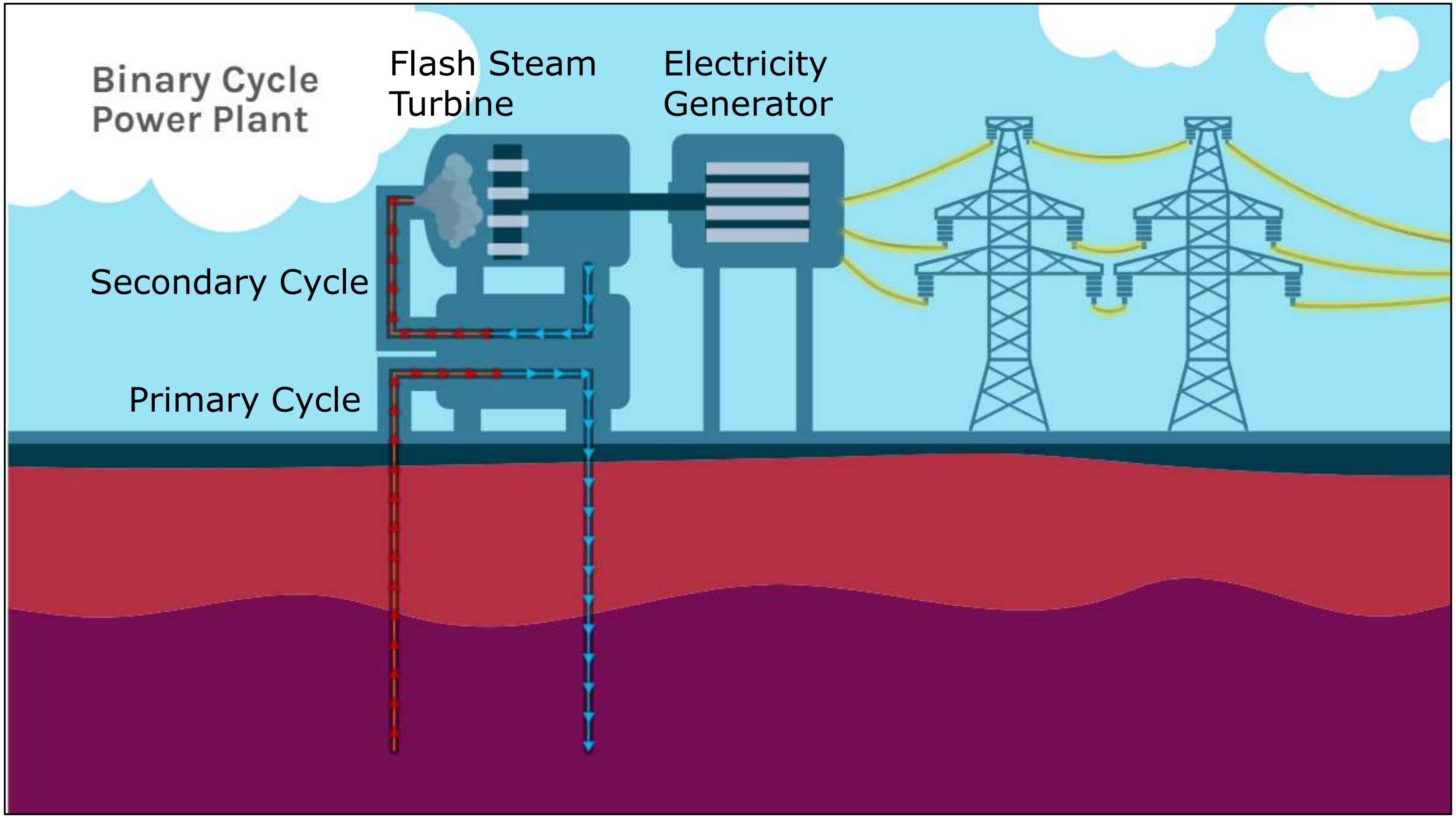
Req. compressor work

$$w = C_{air} \cdot \left(T_{in} - T_{air}\right) - \left|Q_g\right|$$

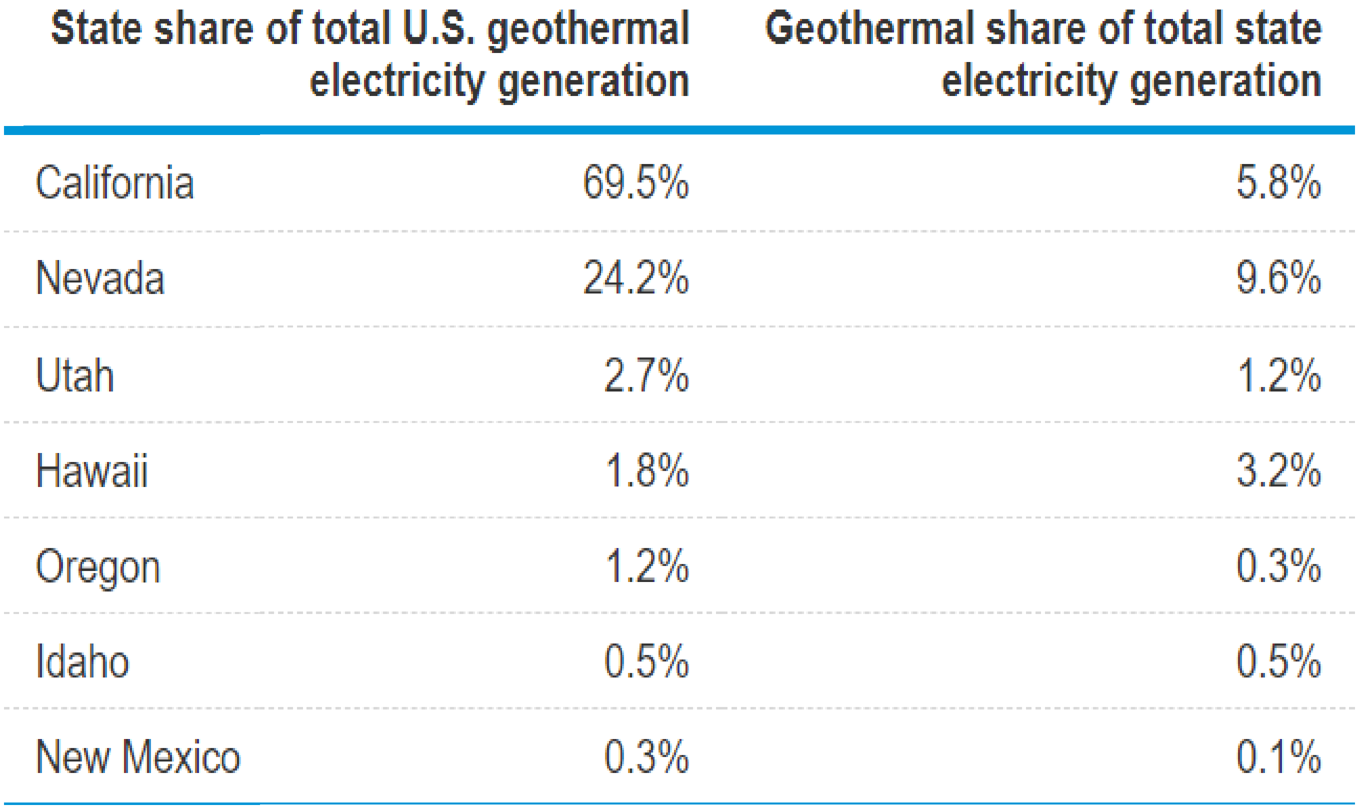


Flash-Steam Power Plant

https://www.energy.gov/eere/geothermal/electricity-generation

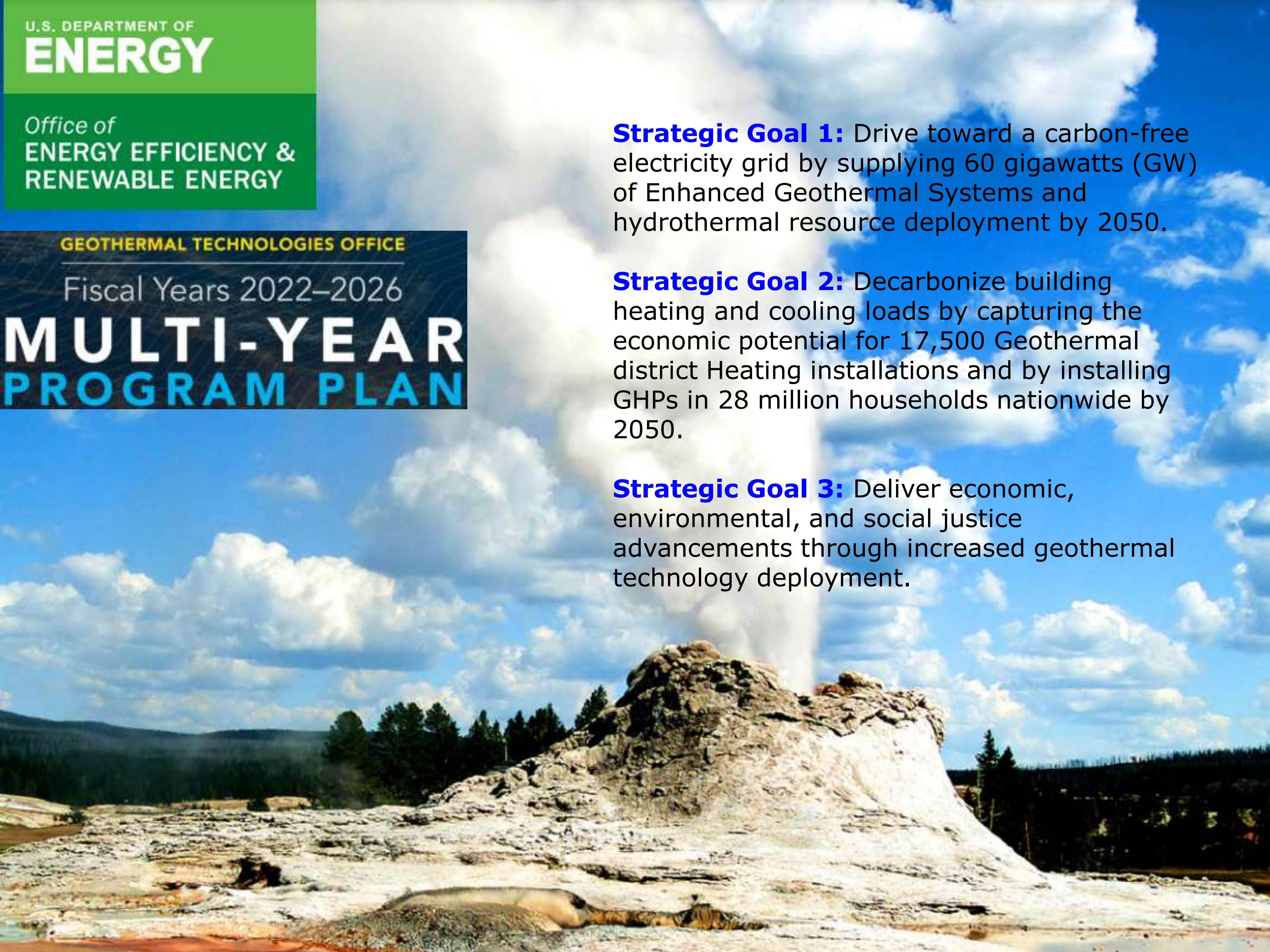


U.S. Geothermal Power Electricity Generation 2022



	State share of total U.S. geothermal electricity generation	Geothermal share of total state electricity generation
California	69.5%	5.8%
Nevada	24.2%	9.6%
Utah	2.7%	1.2%
Hawaii	1.8%	3.2%
Oregon	1.2%	0.3%
Idaho	0.5%	0.5%
New Mexico	0.3%	0.1%

2022: US produced about 17 TWh (17 billion kWh) = 0.4% of total U.S. utility-scale electricity generation.
(Utility-scale power plants: capacity ≥ 1 megawatt ($1MW_e$) of electricity generation)



U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

GEOTHERMAL TECHNOLOGIES OFFICE

Fiscal Years 2022–2026

MULTI-YEAR
PROGRAM PLAN

Strategic Goal 1: Drive toward a carbon-free electricity grid by supplying 60 gigawatts (GW) of Enhanced Geothermal Systems and hydrothermal resource deployment by 2050.

Strategic Goal 2: Decarbonize building heating and cooling loads by capturing the economic potential for 17,500 Geothermal district Heating installations and by installing GHPs in 28 million households nationwide by 2050.

Strategic Goal 3: Deliver economic, environmental, and social justice advancements through increased geothermal technology deployment.