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

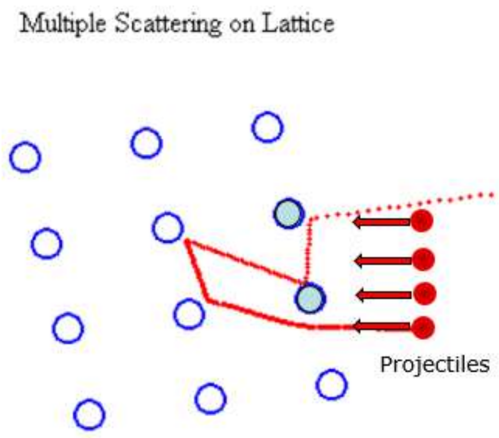
0) Systems in contact equalize mean internal (kinetic) energies,
→ temperatures equalize.
"Canonical & grand canonical" ensembles (of many ident. systems).

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

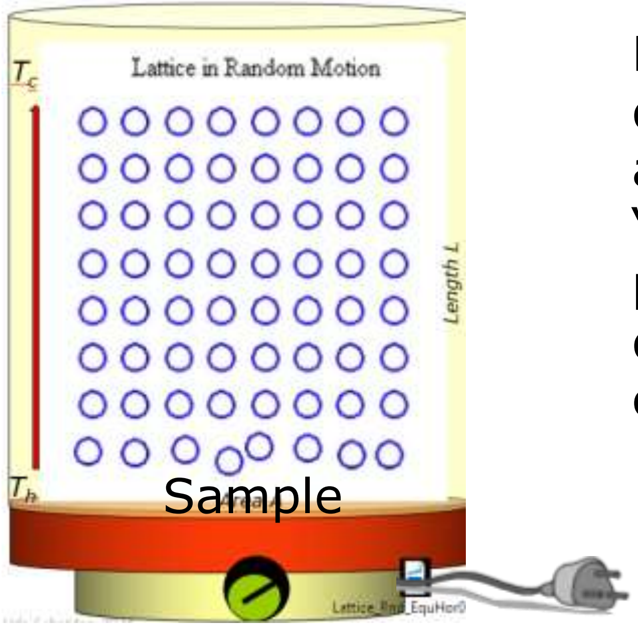
2) Complex systems evolve spontaneously toward state of maximum randomness (complexity)→ Measure=Entropy.

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

Dissipation Processes Produce Equilibrium State



Random pattern of projectile deflections, momenta and energies., the energy of the projectile is dissipated over all particles in the system.

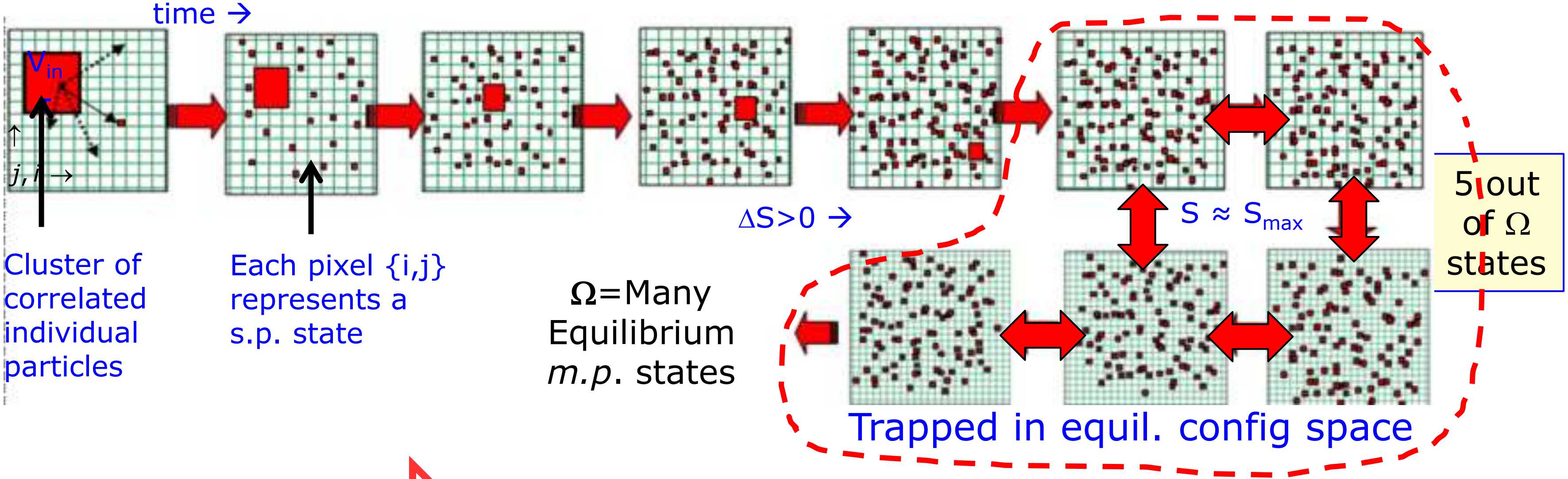


Electrical energy (electron current) is dissipated in hot plate. Resulting energy and/or density disturbances propagate “spontaneously” through solid lattice of plate into sample on the plate. → Energy is distributed “evenly” over all particles in the connected materials.

Quantitative Considerations

Randomization: Spontaneous Dissolution of Cluster

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



time →

V_{in}

↑ *j*, *i* →

Cluster of correlated individual particles

Each pixel {i,j} represents a s.p. state

ΔS>0 →

$S \approx S_{max}$

5 out of Ω states

Ω=Many Equilibrium *m.p*. states

Trapped in equil. config space

Naturally spontaneous

Natural direction of spontaneous process: Number **Ω** of visited multi-particle states increases in time, from simple to complex. ➔ 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. states: *and #m.p.microstates*

"*Entropy*" $\boxed{S := k_B \cdot Ln\ \Omega = -k_B \cdot \sum_{i,j} p_{ij}\ Ln\ p_{ij}}$

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

S= State Function; Boltzmann (1877)

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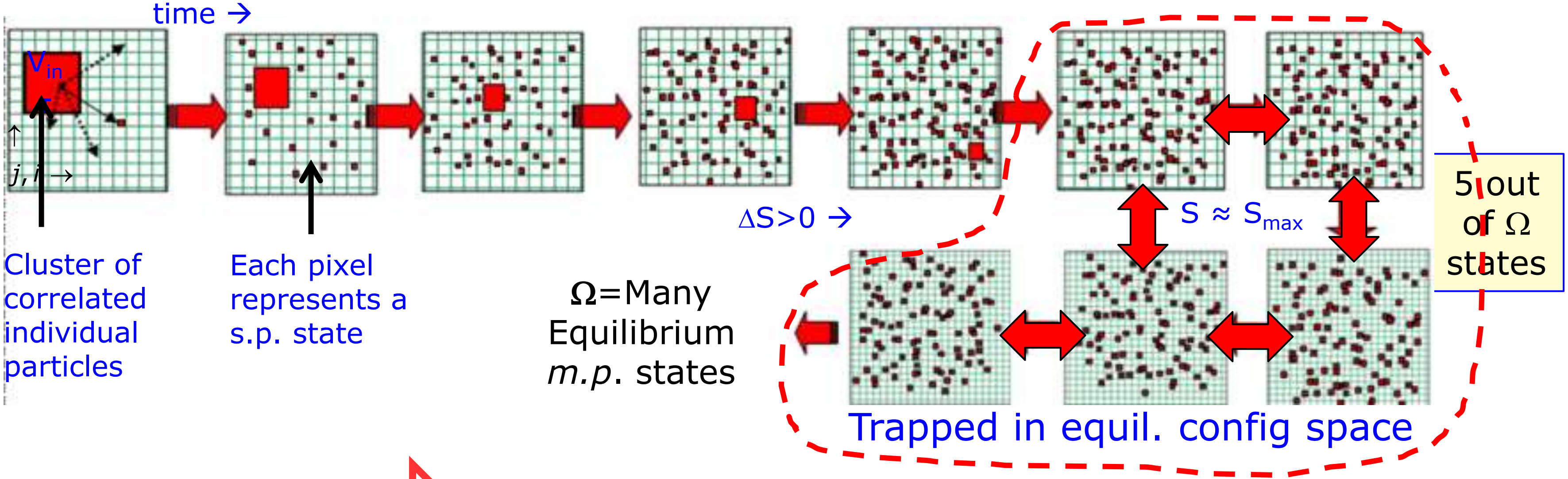

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Quantitative Measure (microscopic)

$$Order: p_{ij} = \{0,1\} \rightarrow S = 0$$

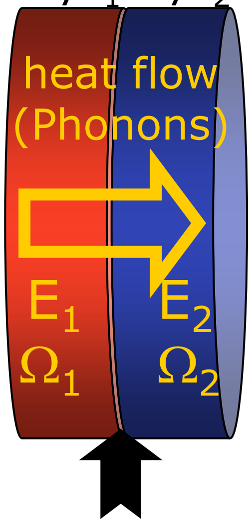
$$Random: p_{ij} = const. \neq \{0,1\} \rightarrow S = S_{max}$$

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

$$2.\,Law\ of\ TD: Entropy\ increases\ in\ spontaneous\ processes$$

Energy Equilibration By Heat Exchange

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



Thermal Contact

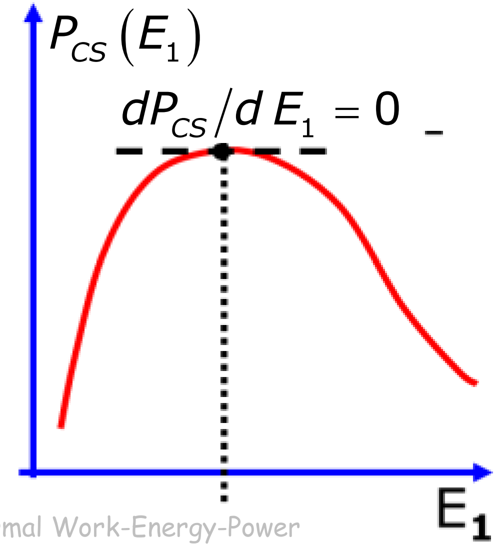
Constant energy $\boldsymbol{E}=E_1+E_2$ → Search for the most likely final energy partition E$_1$/E$_2$. For each spontaneous exchange of heat energy $\Delta q=-\Delta E_1=+\Delta E_2$ → Visited #of states increases → increase in probability P_{CS} to remain trapped in region.

$$\Delta P_{CS}(E,E_1) \propto \Delta\Omega_{CS} = \Delta[\Omega_1(E_1)\cdot\Omega_2(E_2)]$$
$$=[\Delta\Omega_1(E_1)]\cdot\Omega_2(E_2) + \Omega_1(E_1)\cdot[\Delta\Omega_2(E_2)]$$

Ω=visited #states

CS Probability change
with $\Delta E_1 = -\Delta E_2 < 0$

$$\boxed{\frac{\Delta P_{CS}}{\Delta E_1} \propto \frac{\Delta\Omega_1(E_1)}{\Delta E_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{\Delta\Omega_2(E_2)}{\Delta E_2}}$$



Find equilibrium : *Maximize* P_{CS} $\quad \frac{dP_{CS}}{dE_1} = 0 \rightarrow$

$$\boxed{\frac{1}{\Omega_1}\frac{d\Omega_1(E_1)}{dE_1} = \frac{1}{\Omega_2}\frac{d\Omega_2(E_2)}{dE_2}}$$

dimension $[\;] = 1/Energy$

Energy Equilibration By Heat Exchange

W. Udo Schröder, 2024

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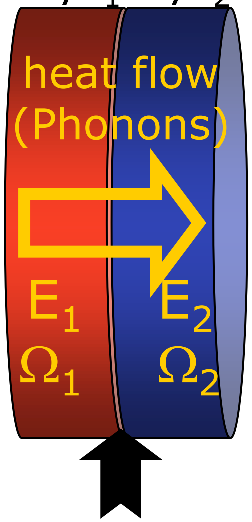

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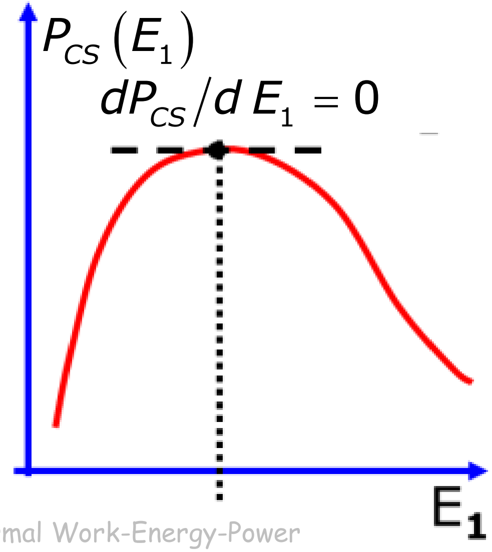
$$Find\ equilibrium: Maximize\ P_{CS}$$

$$\frac{dP_{CS}}{dE_1}=0 \rightarrow \quad \frac{1}{\Omega_1}\frac{d\Omega_1(E_1)}{dE_1}=\frac{1}{\Omega_2}\frac{d\Omega_2(E_2)}{dE_2}$$

dimension
$[\ \ ] = 1/Energy$

Independent of index → independent of material properties 1.2; but common temperature ***T*** depends on the ratio energy/mass.



Plausible Ansatz: $$\frac{d}{dE}\underbrace{Ln\ \Omega(E)}_{=S/k} = const.\underset{mean}{\left(\langle E\rangle_{12}\right)} \propto \frac{1}{kT} \Rightarrow dS(E)/k \propto \frac{dE}{kT}$$

In Equilibrium
dE is reversible

$$\underset{\uparrow = dq\ heat}{dE} = T\cdot dS$$

$$\boxed{dS = \frac{dq}{T} = \frac{Heat}{Temperature}}$$

$$common\ T_1 = T_2 = T$$

Thermodynamic Energies & Driving Potentials

U : *Internal structural energy* of 1mole material :

extensive (additive) state function U

H : *Enthalpy* Structural Energy plus pressure – volume work

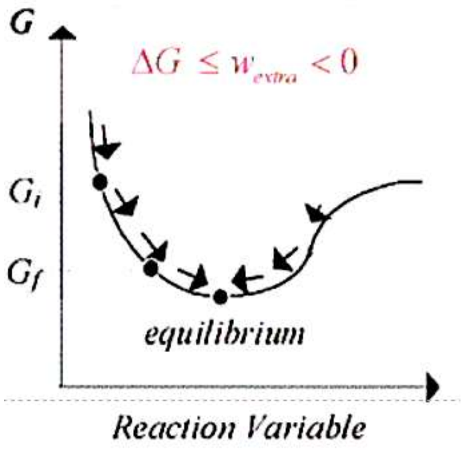
extensive state function $H = U + P \cdot V \rightarrow \Delta H\big|_p = \Delta U + p \cdot dV$

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

$\rightarrow$ large databases; $H^0 = 0$ for pure elemental substances (incl phase)

Example $mix\left(reag1 + reag2\right) \rightarrow H_{mix} = H_{reag1} + H_{reag2}$

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

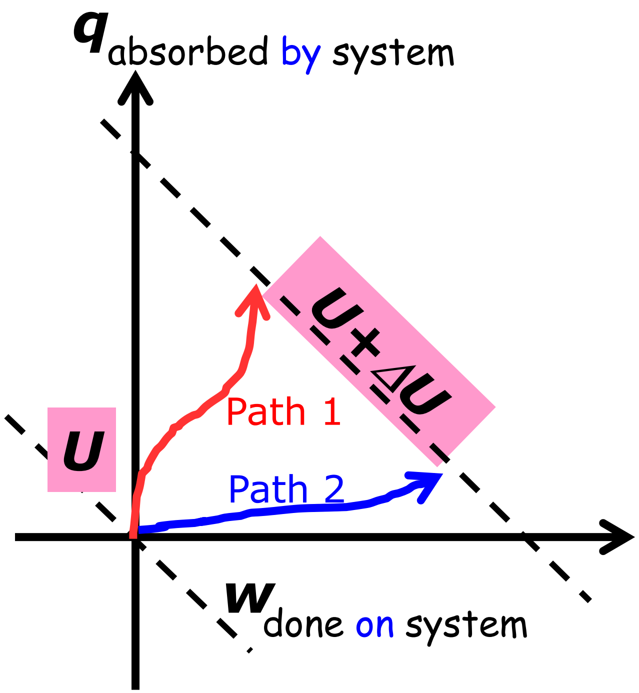
System *will do spontaneously* : $w_{process} = -\Delta A_{process} < 0$

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

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

Equivalence of Work and Heat Energy

First Law of Thermodynamics: Energy ***U*** of an isolated system is conserved.
Isolated System=System+Environment. ***U* is a state function**



If system can exchange energy with environment, it can do that by

1) doing or receiving work ***w*** or by
2) absorbing or emitting heat ***q***.

$$\Delta U = \mathbf{w}+\mathbf{q},$$

→ ***W and q are path functions,***
NOT state functions.

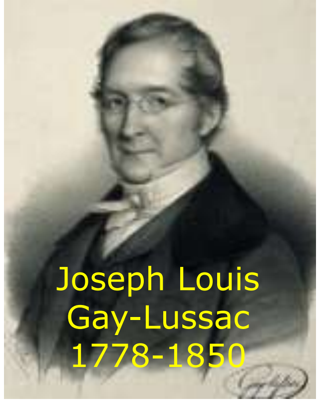
Both are counted positive, if ***U*** is increased

Example: Energy loss suffered is equal to the sum of work done ($w<0$) and heat emitted ($q>0$) by the system.

In equilibrium (long times) ***U*** is distributed randomly over all degrees of freedom. System has no memory about production pathway.

Convert heat energy to mechanical work

Thermodynamics: Ideal-Gas Equations of State EoS



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

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

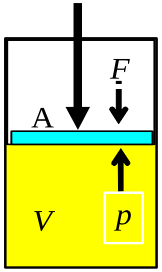
Boyle's Law $P(V) \propto 1/V$ or $\boxed{P \cdot V = const(n,T)}$

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)*

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

Compression



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

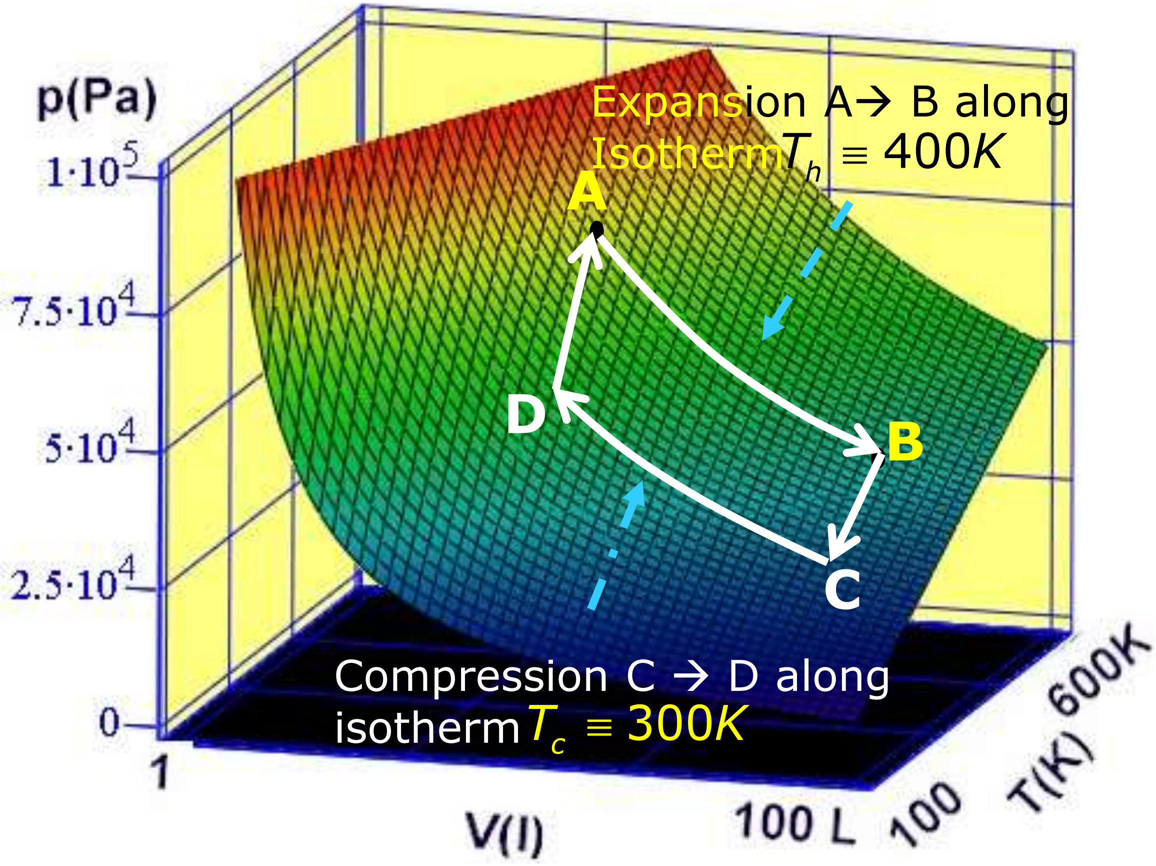
$\gamma = C_P / C_V$ *Specific Heats*

P *or* $V = const$

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

Reversible Circular Processes on EoS Hyperplane

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



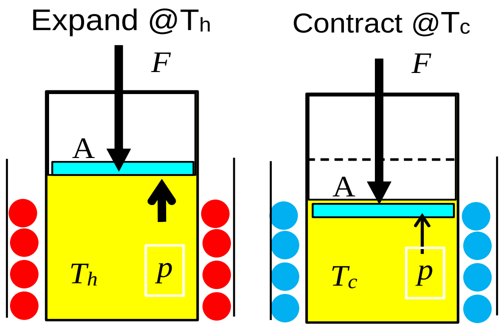
Expansion A→ B along Isotherm $T_h \equiv 400K$

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

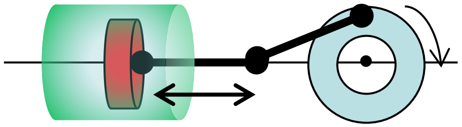
A circular process

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*

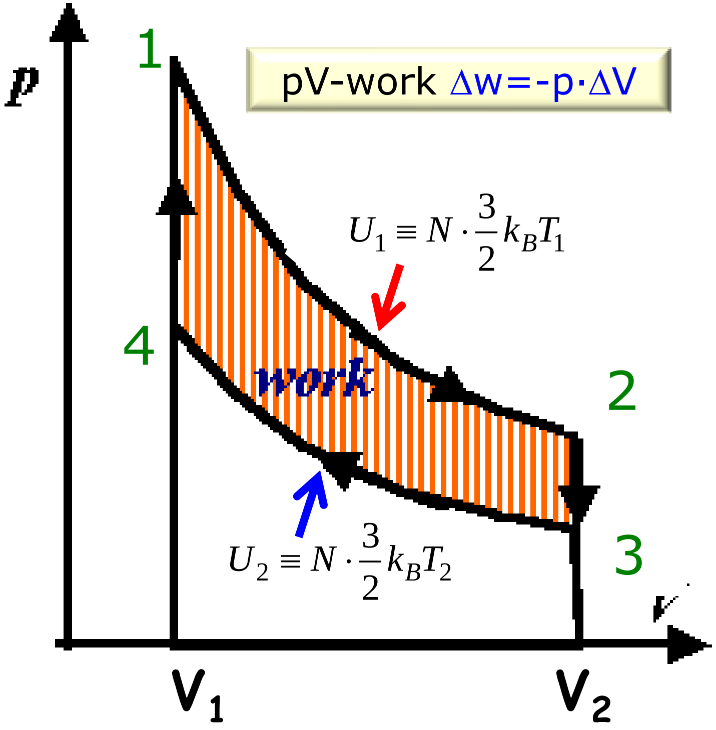
R = 0.0821 liter·atm/mol·K

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



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

Sign convention: Internal energy gain or loss

→ **Work-Heat Balance:**

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

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

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

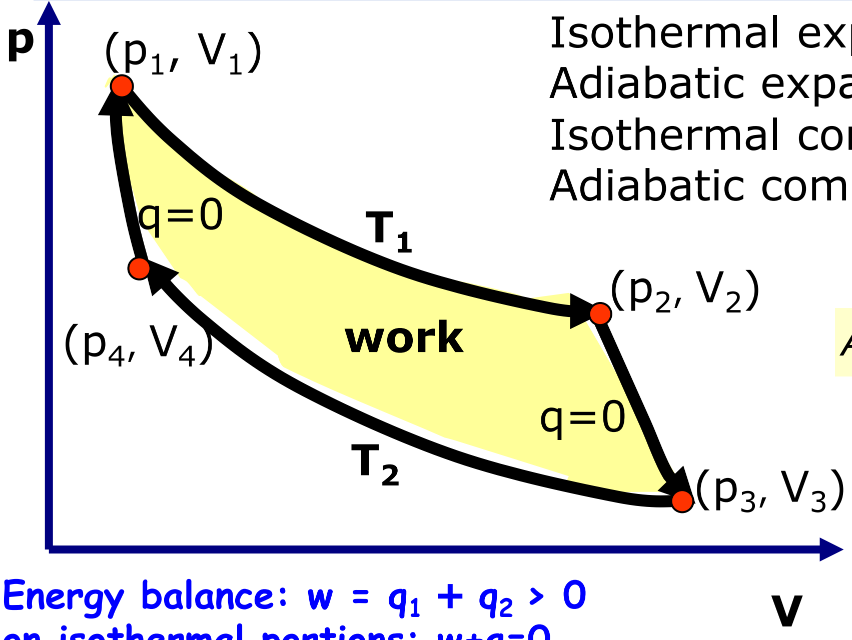
Total work by engine : $w = w_1+ w_2 < 0$

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. → $V_4/V_1 = V_3/V_2$
→ $V_4/V_3 = V_1/V_2$

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.: ΔS = q/T= 0 since q= 0.
Irreversible adiabatic exp./compr.: ΔS ≠ 0.

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

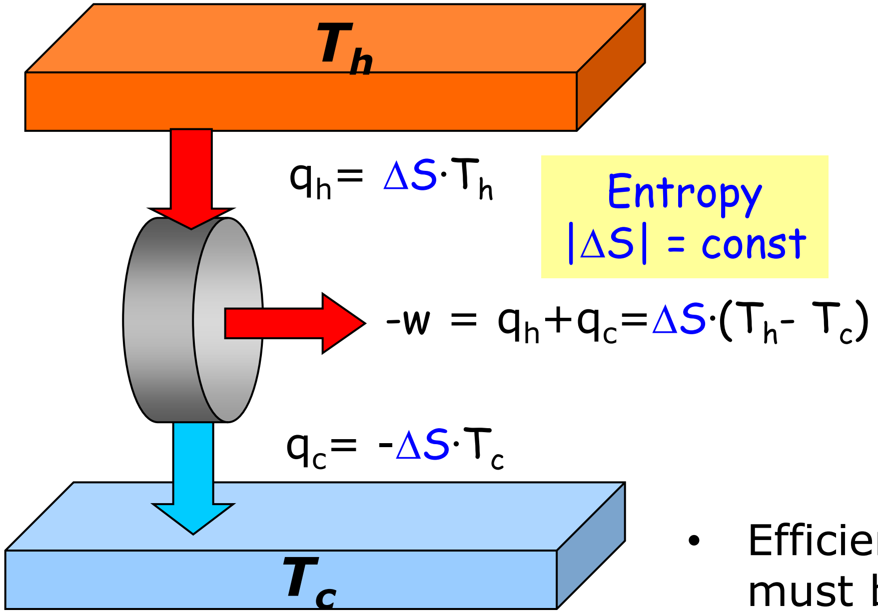
Entropy is conserved in reversible cyclic processes: $\Delta S_1 + \Delta S_2 = 0.$

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

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



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.

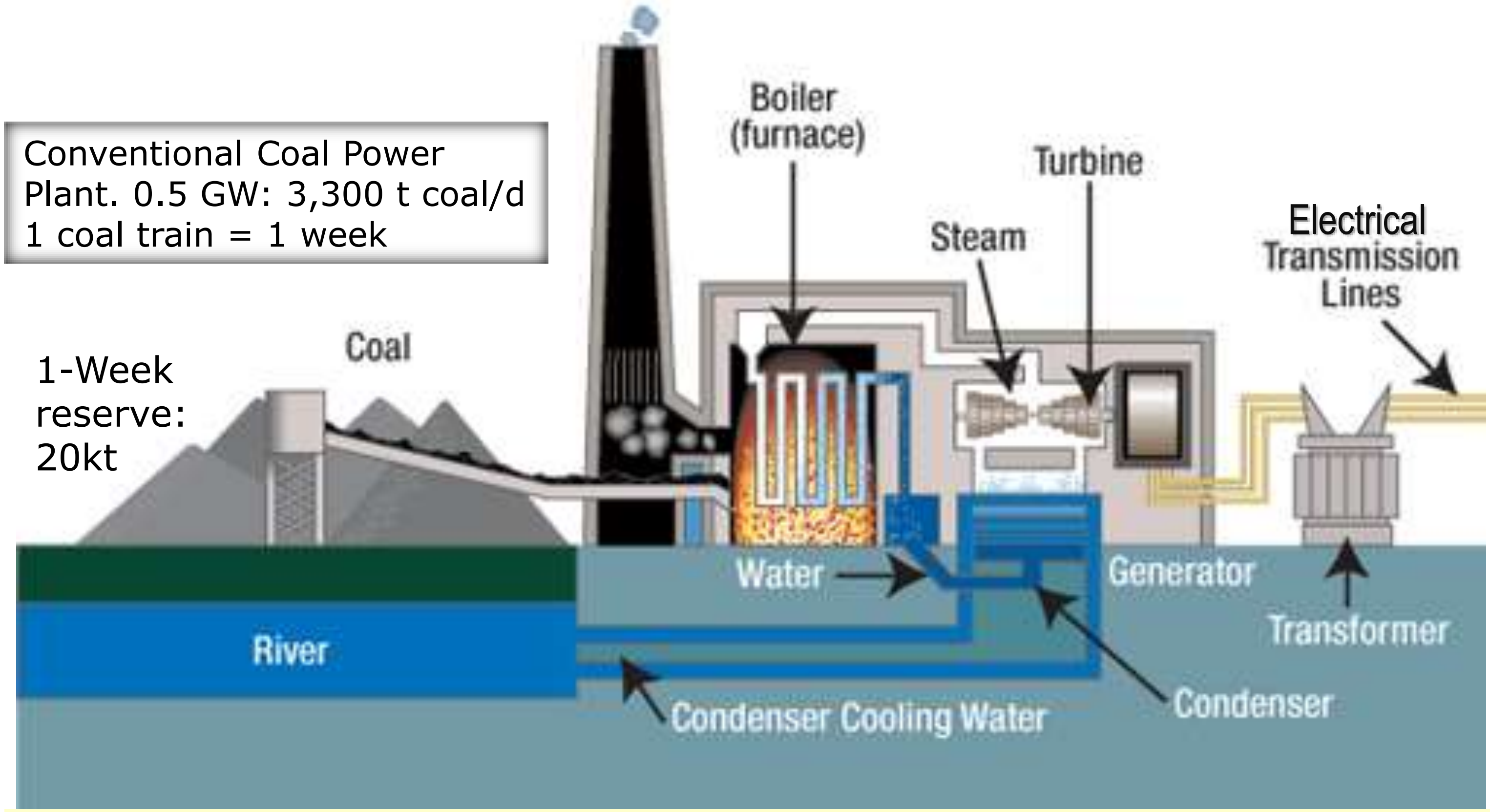
Typical thermal engines have efficiencies of $\boxed{\varepsilon_{therm} \sim 0.3}$.

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 ?

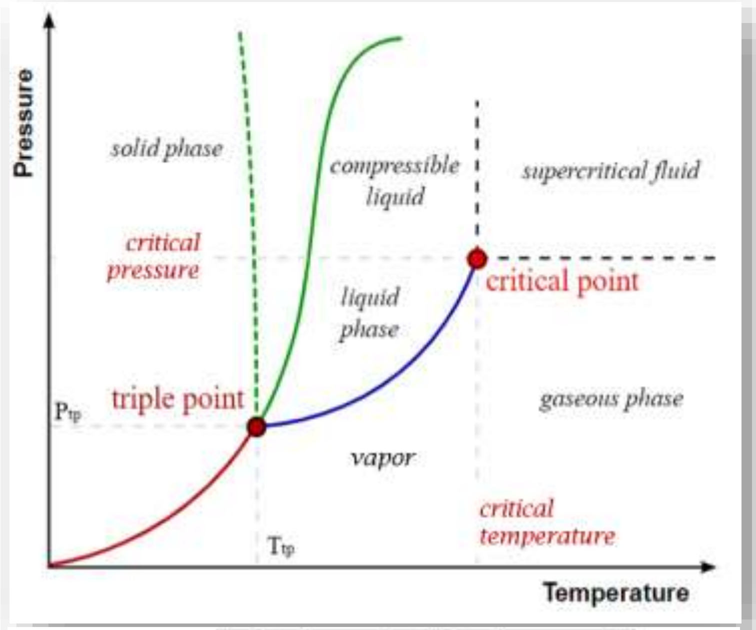
Real Substances (Different Phases: *s*, *ℓ*, *g*, *sc*)

All real substances have distinct physical phases:

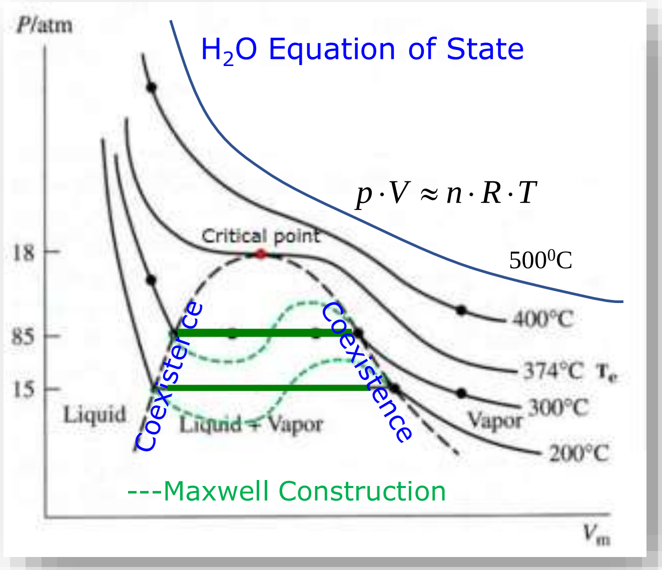
solid ($T<T_{freeze}$), liquid ($T_{freeze}<T< T_{boil}$) and gas ($T_{boil}<T$)

Phase transitions occur upon changes in internal energy by characteristic amounts: *latent heat (Δ-enthalpy) of fusion or latent heat of vaporization*

$$Enthalpy\ \boxed{H = U + P_{ext}\cdot V_{sys}} \qquad at\ P_{ext}: q = \Delta H = C_p \Delta T;\ heat\ capacity\ C_p$$



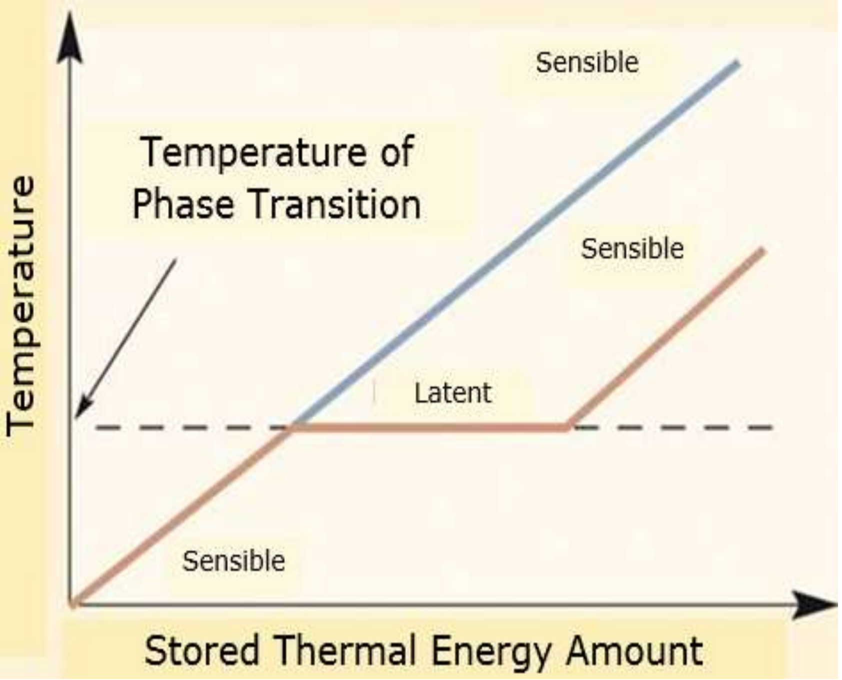
		Critical pressure P_c		Critical temperature T_c		
Material	Formula	psia	bar (abs)	°F	°C	$k = C_p/C_v$
Water	H_2O	3206	221	705	374	1.32



- - - - *van der Waals gas model*

$$\left(p + \frac{n^2\cdot a}{V^2}\right)\cdot\left(V - n\cdot b\right) = n\cdot R\cdot T$$

Thermal Energy Transfer to Storage Materials



Thermal properties

(i) Suitable (medium-*T*) phase-transition temperature.

(ii) High latent heat of transition.

(iii) Good heat transfer.

Recent review of PCM storage materials: A. Sharma et al., Renewable and Sustainable Energy Reviews 13 (2009) 318–345

Physical properties

(i) Favorable phase equilibrium.
(ii) High density.
(iii) Small volume change.
(iv) Low vapor pressure.

Kinetic properties

(i) No supercooling.
(ii) Sufficient crystallization rate.

Chemical properties

(i) Long-term chemical stability.
(ii) High thermal stability
(ii) Compatibility construction materials
(iii) Low toxicity.
(iv) Low fire hazard.

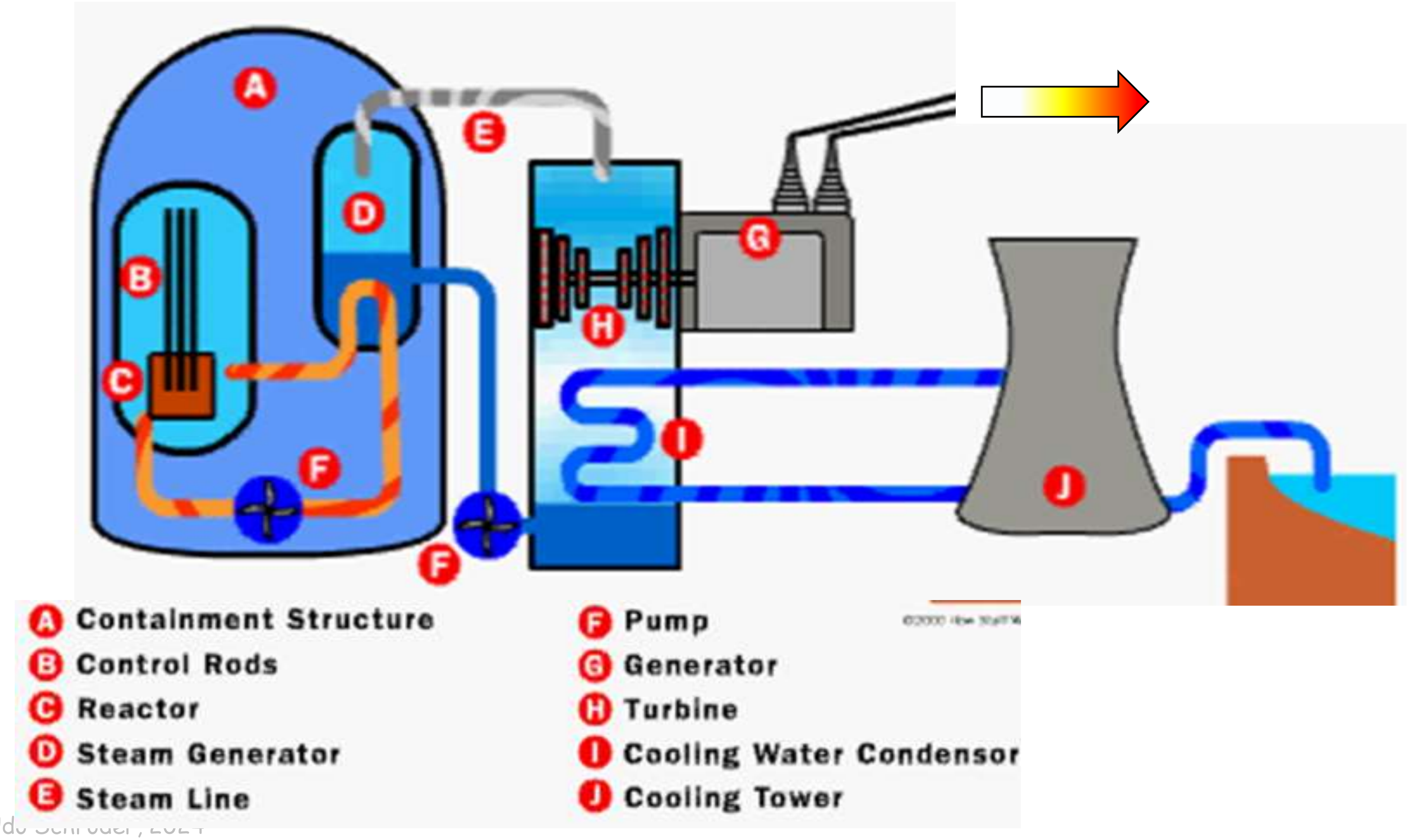
Economics

(i) Abundant.
(ii) Available.
(iii) Cost effective.

Thermal (Nuclear) Power Plant

Reactor safety, spent fuel storage, reprocessing, high-level depository

Conventional Nuclear Power Plant
1.0 GW_e: 20 t U per year



End of
Work, Energy, & Power II