

# Laws of Thermodynamics

1. Energy is conserved, it is neither created nor destroyed  
a.  $dU = TdS - PdV = Q + W$
2. Entropy always increases in the universe  
a.  $dS > \frac{dQ}{T_{surr}}$
3. Entropy is constant at absolute 0°K (pure perfect crystal  $\Rightarrow S = 0$ )  
a.  $S_0 = k_B \ln \ln(1) = 0$
4. Fundamental Equation:  $dU = TdS - PdV + \sum \mu_i dN_i$

## Properties

- Intensive = doesn't change with system size/extent  
○  $T, P, \mu, \rho, c_p/c_v, u, h, g, f, s, v, n, k, C, \text{viscosity}$
- Extensive = changes with system size/extent  
○  $S, V, N, m, C_p/C_v, U, H, G, F$
- Composite = combination of extensive and intensive properties  
○ Ratio of extensive properties = intensive property ( $\rho = \frac{m}{V}$ )  
○ "Specific" =  $\frac{\text{extensive property}}{\text{mass}}$  "Molar" =  $\frac{\text{extensive property}}{\text{mole}} = \text{lowercase}$

**Constants:**  $R = k_B N_A = 8.3144 \frac{J}{K \cdot mol} \left( \frac{m^3 \cdot Pa}{K \cdot mol} \right) \left( \frac{kg \cdot m^2}{s^2 \cdot K \cdot mol} \right) = 0.082057 \frac{L \cdot atm}{K \cdot mol} = 1.987204 \frac{kcal}{K \cdot mol}$

- Boltzmann:  $k_B = 1.380648 \times 10^{-23} \frac{J}{K}$  Avogadro:  $N_A = 6.022140 \times 10^{23} \text{mol}^{-1}$
- STP° = 273.15°K, 1bar =  $10^5 Pa$  Faraday:  $F = 96485.332 \frac{C}{mol}$

## Equations of State & Equilibrium: $f(P, V, T) = 0$

- Ideal:  $PV = nRT = Nk_B T$   $P = CRT$   $PM_W = \rho RT$  Low  $P$ , High  $T$
- Van der Waals, (Soave-)Redlich-Kwong, Peng-Robinson, Virial
- Antoine Equation:  $\ln \ln(P^{sat}) = A - \frac{B}{C+T}$   $A, B, C$  = empirical constants
- Clausius-Clapeyron Equation:  $\frac{dP}{dT} = \frac{s^\beta - s^\alpha}{v^\beta - v^\alpha} = \frac{\Delta H_{vap}}{(v^\beta - v^\alpha)T}$  for phase  $\alpha\beta$  equilibrium
- Fugacity  $f = P$  of Ideal Gas @  $T$  &  $G$  of real gas  $\phi = \frac{f}{P}$  = fugacity coeff
  - "Escaping tendency" different than mechanical, measured pressure
  - Describes chemical equilibrium:  $f_a = f_b$   $\mu_i - \mu_i^\circ = RT \ln \ln \left( \frac{f_i}{f_i^\circ} \right)$
  - Substitute for  $P$  in  $PV = nRT \Rightarrow fV = nRT$  to describe real gases
  - $d\mu = dg = -sdT + vdP \Rightarrow \Delta T = 0, PV = nRT \Rightarrow d\mu = RT d \ln \ln P$
  - $\ln(\phi) = \int_0^P \frac{V - V_{ideal}}{nRT} dP$   $Z = \frac{PV}{nRT} \Rightarrow \ln(\phi) = \int_0^P \frac{Z-1}{P} dP$
  - Condensed phases  $\Rightarrow$  Poynting:  $f = \phi_{sat} P_{sat} e^{\frac{V(P-P_{sat})}{RT}}$  because  $f_{g,sat} = f_{l,sat}$
  - Lewis Fugacity rule:  $\phi_{i,pure} = \phi_{i,in mixture} \Rightarrow f_{i,pure} = y_i f_{i,in mixture}$
- Activity  $a_i = \exp \exp \left( \frac{\mu_i - \mu_i^\circ}{RT} \right) = \gamma_i x_i = \frac{f_i}{P^\circ}$   $\gamma_i$  = activity coeff  $a_{solid,liquid} = 1$ 
  - "Effective concentration" of a species in a mixture/reaction
  - Akin to chemical potential in theory but used differently
  - Integrate fugacity:  $d\mu = RT d \ln \ln P \Rightarrow \mu_i = \mu_i^\circ - RT \ln \ln(a_i)$
  - Substitute for  $C$  in  $K = \frac{C_C C_D}{C_A C_B}$  or  $r = k C_A^n$  to describe real solutions

**Caloric Theory** = obsolete theory that heat is a self-repellent fluid called caloric that could be attached to matter and later released from it

**Bridgeman** = organization of 28 elementary thermodynamic equations. Shows how  $T, P, V, S, U, H, G, F$  change with each held constant

## **Fundamental Parameters**

- **Conjugate Variables:**  $(T, S)$   $(P, V)$   $(\mu, N)$  (*force, displacement*) (*intensive, extensive*)
  - $T * S = Q [=] J \Rightarrow T$  gradients drive  $S$  change
    - Energy conservation, thermodynamics
  - $P * V = W [=] J \Rightarrow P$  gradients drive  $V$  change
    - Momentum conservation, fluid dynamics
  - $\mu * N = M [=] J \Rightarrow \mu$  gradients drive  $N$  change
    - Mass conservation, chemistry
- **Temperature**  $T [=] ^\circ K, ^\circ C, ^\circ F, ^\circ R$ 
  - Measure of submicroscopic motions and vibrations (NOT heat)
  - Thermal equilibrium  $\Rightarrow T_{sys} = T_{surr}$
- **Entropy**  $S [=] \frac{J}{K}$ 
  - Measure of disorder, always increasing in universe
  - $S = k_B \ln \ln(\Omega)$ ,  $\Omega$  = number of microstates
  - Only measured indirectly through Maxwell Relations
  - At equilibrium entropy is at a maximum
- **Pressure**  $P [=] \frac{J}{m^3} = Pa = \frac{N}{m^2} = \frac{kg}{m*s^2}, bar, atm, mmHg$ 
  - Force applied over area, normal stress
  - Mechanical equilibrium  $\Rightarrow P_{sys} = P_{surr}$
- **Volume**  $V [=] m^3 = \frac{J}{Pa}, L, ft^3$ 
  - Measure of physical space taken up by matter (NOT empty space)
- **Chemical Potential**  $\mu [=] J$  (NOT chemical potential energy)
  - Energy changed through chemical reaction/phase transition
  - $\mu = \left(\frac{dU}{dN}\right)_{S,V,N} = \left(\frac{dH}{dN}\right)_{S,P,N} = \left(\frac{dG}{dN}\right)_{T,P,N} = \left(\frac{dF}{dN}\right)_{T,V,N}$
  - Molecules move down chemical potential gradients (like gravity)
  - Diffusive equilibrium  $\Rightarrow \mu_{sys} = \mu_{surr}$
- **Composition**  $N [=] \#, unitless$ 
  - Measure of the number of particles in a system
  - $N [=] \# \quad n = \frac{N}{N_A} [=] mol$

# Thermodynamic Potentials

Definitions change based on context/process under consideration

$\{x, y, z\}$  = natural variables (held constant  $\Rightarrow$  potential =  $W_{\max \text{ useful}}$ )

- **Internal Energy**  $f\{S, V, N\}$ 
  - $dU = TdS - PdV + \sum \mu_i dN_i$   $U = TS - PV + \sum \mu_i N_i$   $\Delta U = Q + W_{PV} + W_{Isochoric}$
  - Described explicitly by microscopic energies...
    - kinetic (translation, rotation, vibration)
    - potential (chemical, electrical, nuclear)
  - $dU(T, V) = C_V dT + \left(T\left(\frac{dP}{dT}\right)_V - P\right) dV$
  - $dU(T, P) = (C_P - \alpha PV) dT + (\beta_T P - \alpha T) V dP$
  - Ideal Gas:  $U = \frac{3}{2} nRT$
- **Enthalpy**  $f\{S, P, N\}$ 
  - $dH = TdS + VdP + \sum \mu_i dN_i$   $H = TS + \sum \mu_i N_i = U + PV$   $\Delta H = Q + W_{Isochoric}$
  - The energy to create system plus the work to make room for it  
 $dH = d(U + PV)$
  - @  $dP = 0 \Rightarrow \Delta H =$  heat from chemical reaction and external heat transfer
    - $\Delta H = + \Rightarrow$  endothermic reaction,  $- \Rightarrow$  exothermic reaction
  - $dH(T, P) = C_P dT + V(1 - \alpha T) dP$
  - Enthalpy of... formation, rxn, vap, fus, sol, combustion, mix
- **Gibbs Energy**  $f\{T, P, N\}$ 
  - $dG = -SdT + VdP + \sum \mu_i dN_i$   $G = \sum \mu_i N_i = H - TS$   $\Delta G = \Delta H - T\Delta S = W_{Isochoric}$
  - Chemical reaction spontaneity:  $\Delta T = 0, \Delta P = 0 \Rightarrow$  only  $\Delta \mu \neq 0$  can vary
    - $\Delta G = - \Rightarrow$  spontaneous,  $+ \Rightarrow$  non-spontaneous,  $0 \Rightarrow$  equilibrium
  - $\Delta G^\circ_R = -RT \ln(K_{eq})$   $\Delta G^\circ_R = -nFE^\circ$   $E^\circ = \text{Standard cell potential} [=] \frac{J}{C} = V$
  - **Gibbs-Duhem**:  $0 = -SdT + VdP + \sum N_i d\mu_i$
- **Helmholtz Energy**  $f\{T, V, N\}$ 
  - $dF = -SdT - PdV + \sum \mu_i dN_i$   $F = -PV + \sum \mu_i N_i = U - TS$   $\Delta F = \Delta U - T\Delta S = W_{PV} + W_{Isochoric}$
  - Chemical reaction spontaneity:  $\Delta T = 0, \Delta V = 0 \Rightarrow$  only  $\Delta \mu \neq 0$  can vary
    - $\Delta F = - \Rightarrow$  spontaneous,  $+ \Rightarrow$  non-spontaneous,  $0 \Rightarrow$  equilibrium
- $d(PV) = d(H - U) = d(G - F)$   $d(TS) = d(U - F) = d(H - G)$
- **Exergy (Availability)**
  - $B = U - T_R S + P_R V - \sum \mu_{i,R} N_i$   $B = H - T_R S$   $B = F + P_R V$   $B = G$
  - Exergy = U + heat/entropic loss + available PV work + available chemical energy
  - Measures how far system is from equilibrium with surroundings
    - A system in equilibrium with its surroundings has 0 exergy
  - Describes amount of available work in a system (usefulness of streams in chemical plant)
- **Free Energy**: energy that is readily released/freed ( $G, F$ )
- **Free Entropy**: entropy that is readily released/freed

- Helmholtz Free Entropy (Massieu Potential) [ $\Phi$ ]

- $\Phi = -\frac{F}{T} = S - \frac{1}{T}U$   $f\{\frac{1}{T}, V, N\}$

- Gibbs Free Entropy (Planck Potential) [ $\mathcal{E}$ ]

- $\mathcal{E} = -\frac{G}{T} = \Phi - \frac{P}{T}V$   $f\{\frac{1}{T}, \frac{P}{V}, N\}$

- **Grand Potential**  $f\{T, V, \mu\}$

- $d\Phi_G = -SdT - PdV - Nd\mu$   $\Phi_G = -PV$

- The energy extractable from a system by shrinking it to nothing

- **Theoretical Potentials**

- Potential 6  $f\{S, P, \mu\}$

- $dP_6 = TdS + VdP - Nd\mu$   $P_6 = TS$

- The energy extractable from a system by cooling it into perfect crystal?

- Potential 7  $f\{S, V, \mu\}$

- $dP_7 = TdS - PdV - Nd\mu$   $P_7 = TS - PV$

- $\Delta P_7 = \Delta P_6 - \Delta\Phi_G$

- Potential 8  $f\{T, P, \mu\}$

- $dP_8 = -SdT + VdP - Nd\mu$   $P_8 = 0$

# Energy Transfer

Path Dependent: Area under curve on graph, so curve matters, not just ends

- Heat

- Thermal energy transfer (NOT temperature)
- $dQ = TdS$                        $Q = mC_p\Delta T$                       Heat Equation:  $\frac{dT}{dt} - \alpha \nabla^2 T = 0$
- TS Diagram, area under/enclosed by curve is  $Q$ 
  - Graph isobars & isochors for all fundamental parameters
- Sensible heat =  $\Delta T$ , Latent heat = phase change ( $\Delta T = 0$ )

- Work

- Mechanical energy transfer
- $dW = PdV$                        $W = Fd = PA_s$                       Wave Equation:  $\frac{d^2u}{dt^2} - c^2 \nabla^2 u = 0$
- PV Diagram: area under/enclosed by curve is  $W$ 
  - Graph isotherms & adiabats for all fundamental parameters
- $W_{PV} = W_{reversible} = \text{Mechanical work}$ 
  - Volume change ( $\Delta V$ ) caused by gradient between system pressure and external pressure ( $P$ )
  - Can be performed by system on surroundings or by surroundings on system
- $W_{isochoric} = W_{shaft} = W_{irreversible} = \text{Non-mechanical work}$ 
  - No volume change, like pushing a viscous fluid or friction
  - Only performed on sys by surr, never on surr by sys

# Processes/Systems

Model complex processes by series of these processes

Heat reservoir (water bath)  $\approx$  Pressure reservoir (atmosphere)

- **Isothermal**  $\Delta T = 0$ 
  - $Q_{\Delta T=0} = T\Delta S = -W_{\Delta T=0} = -RT \ln \ln \left( \frac{V_2}{V_1} \right) = -RT \ln \ln \left( \frac{P_1}{P_2} \right)$
  - $\Delta U = 0$   $\Delta U_{IG} = f(T) \neq f(P, V)$  IG:  $P = \frac{nRT}{V}$  isotherms on PV graph
  - Phase transitions are isothermal
- **Isobaric**  $\Delta P = 0$ 
  - $Q_{\Delta P=0} = \Delta H = C_P \Delta T$   $W_{\Delta P=0} = P\Delta V = R\Delta T$   $\Delta U = Q - W = C_V \Delta T$
- **Isochoric**  $\Delta V = 0$ 
  - $Q_{\Delta V=0} = \Delta U = C_V \Delta T$   $W_{PV, \Delta V=0} = 0$   $W_{isochoric, \Delta V=0} = \Delta U - Q$
- **Adiabatic**  $Q = 0$ 
  - $\Delta U = W = PdV = RdT$   $\Delta T = ???$
  - Rapid processes are often idealized as adiabatic
  - Graphic adiabat = curve of constant entropy
- **Isentropic**  $\Delta S = 0$ 
  - $dU = C_V dT = PdV$   $dH = C_P dT = VdP$
  - Compressors, Turbines, Pumps...  $\eta_{isentropic} = \frac{W_{actual}}{W_{ideal}} \parallel \frac{W_{ideal}}{W_{actual}} = \frac{H_{2,s} - H_1}{H_2 - H_1}$ 
    - Either only  $W_{PV}$  (**Reversible** adiabatic  $\subset$  Isentropic)...
    - Or  $W_{PV} + W_{isochoric}$  and  $Q$  necessary to oppose  $W_{isochoric}$
- **Isenthalpic**  $\Delta H = 0$ 
  - **Irreversible** adiabatic
  - Throttling (**Joule-Thomson effect**)
    - $\mu_{JT} = \left( \frac{dT}{dP} \right)_H = \frac{V}{C_P} (\alpha T - 1)$   $\mu_{JT, ideal} = 0$
    - $+\mu_{JT} \Rightarrow +\Delta T$ ,  $-\mu_{JT} \Rightarrow -\Delta T$ , divided by  $T_{inversion}$
- **Polytropic**  $PV^n = const$ 
  - Processes that can change all fundamental parameters  $T, P, V, S$
  - $n=0 \Rightarrow$  isobaric  $n=1 \Rightarrow$  isothermal
  - $n=\infty \Rightarrow$  isochoric  $n=\gamma \Rightarrow$  isentropic/adiabatic
  - $1 < n < \gamma \Rightarrow$  heat and work in opposite directions
  - $\gamma < n < \infty \Rightarrow$  heat and work in same direction
- **Systems**
  - **Open** ( $m, Q, W$ ) **Closed** ( $Q, W$ )
  - **Isolated** ( $\quad$ ) Equilibrium  $\Rightarrow S$  is maximized
    - **Thermally Isolated** ( $W$ ) insulated, adiabatic
    - **Mechanically Isolated** ( $Q$ ) rigid
- Changes

◦ Heating	= heat addition	= $+Q$	= $+T, +P, +V, +S$
◦ Cooling	= heat rejection	= $-Q$	= $-T, -P, -V, -S$
◦ Compression	= volume increase	= $+W$	= $+T, +P, -V, -S$
◦ Expansion	= volume reduction	= $-W$	= $-T, -P, +V, +S$

# Material Properties

- **Heat Capacity**

- Measures relative temperature change in response to applied heat
- Measures capacity to store energy absorbed as heat (not conductivity)
- $C = \frac{dQ}{dT} [=] \frac{kg*m^2}{s^2*K} = \frac{J}{K}$        $C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V = \frac{T}{N} \left(\frac{dS}{dT}\right)_V$        $C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P = \frac{T}{N} \left(\frac{dS}{dT}\right)_P$
- $C_P - C_V = VT \frac{\alpha^2}{\beta_T}$       Ideal  $C_P - C_V = R$        $\frac{C_P}{C_V} = \gamma = \frac{\beta_T}{\beta_S}$

- **Compressibility Coefficient**

- Measures volume change in response to a pressure change
- $\beta_T = -\frac{1}{V} \left(\frac{dV}{dP}\right)_{T,N} = -\frac{1}{V} \frac{d^2G}{dP^2}$        $\beta_S = -\frac{1}{V} \left(\frac{dV}{dP}\right)_{S,N} = -\frac{1}{V} \frac{d^2H}{dP^2}$
- $\beta_S = \beta_T - \frac{\alpha^2 T}{\rho C_P}$        $\frac{\beta_T}{\beta_S} = \gamma = \frac{C_P}{C_V}$        $\beta [=] \frac{m^2}{N} = Pa^{-1}$

- **Thermal Expansion Coefficient**

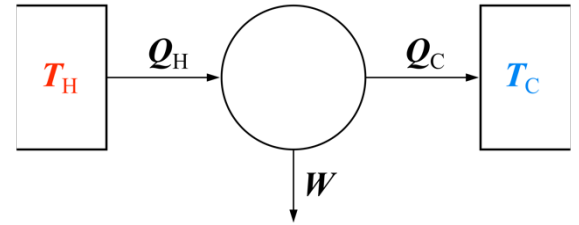
- Measures volume change in response to a temperature change
- $\alpha = \frac{1}{V} \left(\frac{dV}{dT}\right)_{P,N} = \frac{1}{V} \frac{d^2G}{dPdT} = \alpha_V$        $\alpha_L = \frac{1}{L} \left(\frac{dL}{dT}\right)_{P,N}$        $\alpha_A = \frac{1}{A} \left(\frac{dA}{dT}\right)_{P,N}$        $\alpha [=] K^{-1}$

# Thermodynamic Cycles

$$\Delta U_{\text{cycle}} = U_{1-2} + U_{2-3} + U_{3-4} + U_{4-1} = 0$$

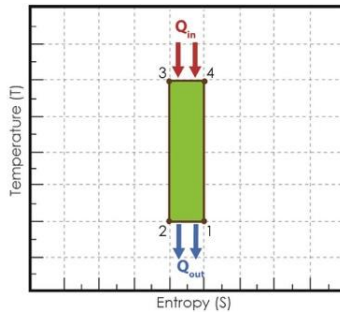
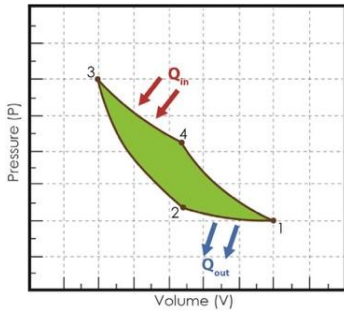
$$\text{Heat Engine} \quad = Q \Rightarrow W = \eta = W/Q_H$$

$$\text{Heat Pump/Refrigerator} \quad = W \Rightarrow Q = \eta = Q_C/W$$



## Carnot

- 1  $+W_{\Delta T=0}$  2  $+W_{\Delta S=0}$  3  $-W_{\Delta T=0}$  4  $-W_{\Delta S=0}$  ↺

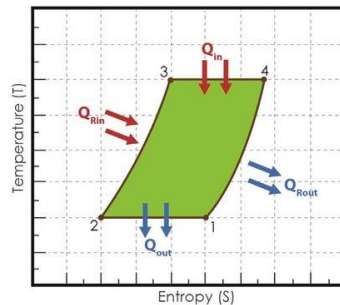
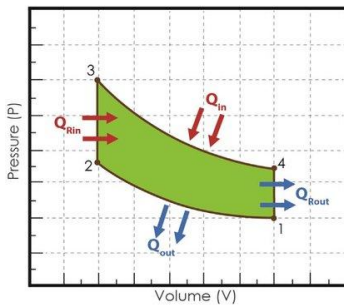


- Theoretical ideal cycle
- Most efficient heat engine/pump

- $W_{12,34} = RT_{1,3} \ln \ln \left( \frac{V_{2,4}}{V_{1,3}} \right)$   $W_{23,41} = C_V \Delta T_{23,41}$
- $Q_{12,34} = -W_{12,34}$   $Q_{23,41} = 0$
- $\eta = \frac{W_{\text{expansion}}}{Q_{\text{heating}}} = \frac{Q_{12} - Q_{34}}{Q_{12}} = 1 - \frac{T_C}{T_H}$   $\frac{V_1}{V_2} = \frac{V_4}{V_3}$

## Sterling

- 1  $-Q_{\Delta T=0}$  2  $+Q_{\Delta V=0}$  3  $+Q_{\Delta T=0}$  4  $-Q_{\Delta V=0}$  ↺

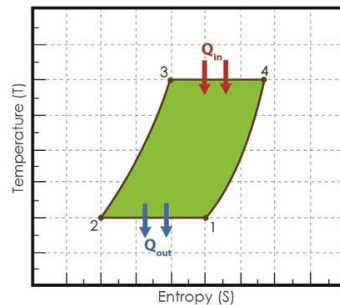
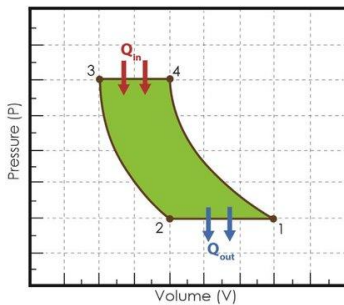


- Ideal cycle
- In practice stages overlap
- Produces Simple Harmonic Motion

- $W_{12,34} = RT_{1,3} \ln \ln \left( \frac{V_{2,4}}{V_{1,3}} \right)$   $W_{23,41} = 0$
- $Q_{12,34} = -W_{12,34}$   $Q_{23,41} = C_V \Delta T_{23,41}$
- $\eta = 1 - T_1/T_2 = 1 - (V_2/V_1)^{\gamma-1}$

## Ericsson

- 1  $+W_{\Delta T=0}$  2  $+Q_{\Delta P=0}$  3  $-W_{\Delta T=0}$  4  $-Q_{\Delta P=0}$  ↺



- Ideal cycle (Ideal Brayton cycle)
- <<<PV diagram: stage = shown - 1

- $W_{12,34} = RT_{1,3} \ln \ln \left( \frac{V_{2,4}}{V_{1,3}} \right)$   $W_{23,41} = P \Delta V = R \Delta T$
- $Q_{12,34} = -W_{12,34}$   $Q_{23,41} = C_P \Delta T_{23,41}$
- $\eta = 1 - T_1/T_2 = 1 - (P_1/P_2)^{(\gamma-1)/\gamma}$

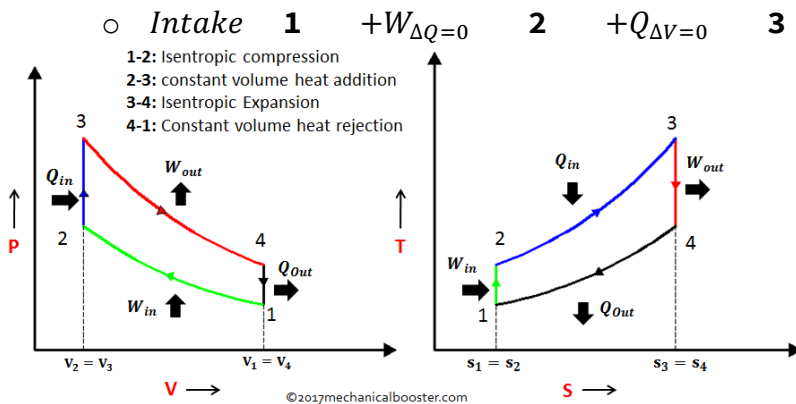
**Regenerator** = Heat exchanger that stores heat temporarily in thermal storage medium before transferring again. Recycles heat in a cycle

**Intercooler** = cools working fluid between compression stages, decreasing the amount of work required and making compressor/pump more isothermal

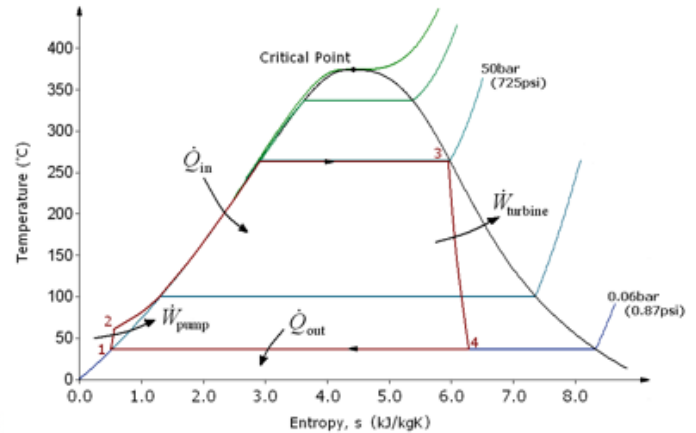
**Reheater** = reheats working fluid between expansion stages, increasing the amount of work output and making turbine more isothermal

## Otto ( $Q, V$ )





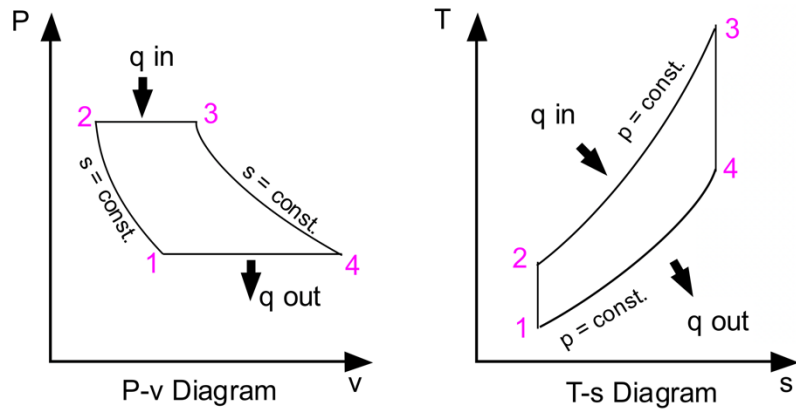
- Internal Combustion Engines
- Automobile Engines
- $\eta = 1 - T_1/T_2 = 1 - (V_2/V_1)^{\gamma-1}$



- **Rankine** ( $Q, P$ )

- $+W_{Q=0} + Q_{\Delta P=0} - W_{Q=0} - Q_{\Delta P=0} \quad \eta = \frac{W_{turbine}}{Q_{boiler}}$
- Steam power plants, nuclear
- Exploits phase change  $\Delta V$
- Pump, Boiler, Turbine, Condenser
- Alt: Superheat steam

- **Brayton** ( $Q, P$ )

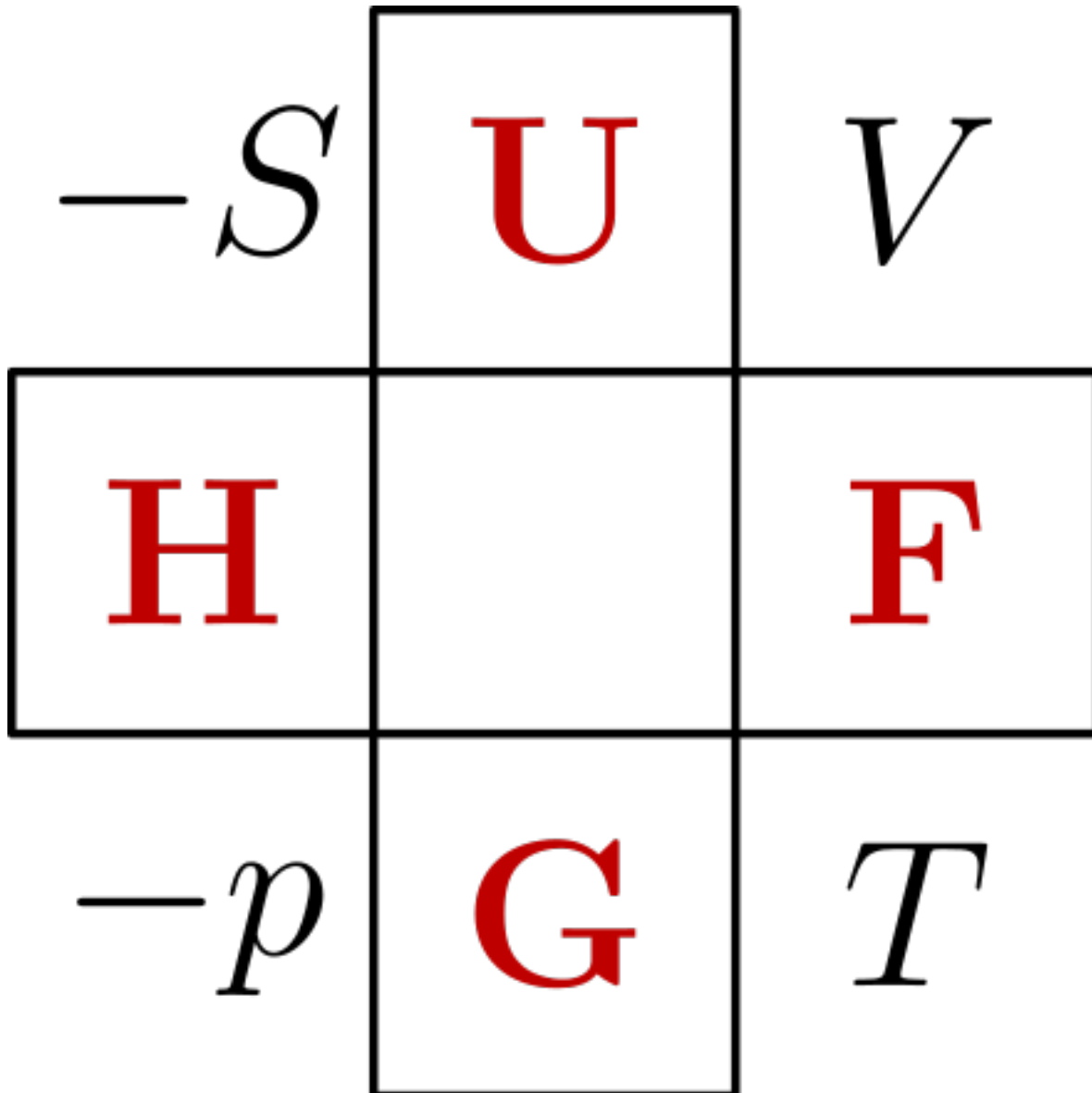


- $+W_{Q=0} + Q_{\Delta P=0} - W_{Q=0} - Q_{\Delta P=0}$
- $\eta = 1 - T_1/T_2 = 1 - (P_1/P_2)^{(\gamma-1)/\gamma}$
- Jet engines,  $\Delta P = 0$

## Etymology

- (Latin) = *calor*  $\Rightarrow$  *heat*  $\Rightarrow$  *caloric, calorie*
- (Latin) = *fugere*  $\Rightarrow$  *to flee*  $\Rightarrow$  *fugacity*
- *εν~* = *en~*  $\Rightarrow$  *within, internal*
  - *θάλπειν* = *thalpein*  $\Rightarrow$  *to heat*  $\Rightarrow$  *enthalpy*
  - *ἔργον* = *ergon*  $\Rightarrow$  *work*  $\Rightarrow$  *energy*
  - *τροπή* = *trope*  $\Rightarrow$  *transform*  $\Rightarrow$  *entropy*
    - *πολύς* = *polus*  $\Rightarrow$  *many*  $\Rightarrow$  *polytropic*
- *ἴσο~* = *iso~*  $\Rightarrow$  *same*
  - *θέρμη* = *therme*  $\Rightarrow$  *heat*  $\Rightarrow$  *isothermal*
    - *δυναμῖς* = *dynamis*  $\Rightarrow$  *power, strength*  $\Rightarrow$  *thermodynamics*
  - *βάρος* = *baros*  $\Rightarrow$  *weight*  $\Rightarrow$  *isobaric*
  - *χωρὸς* = *choros*  $\Rightarrow$  *space*  $\Rightarrow$  *isochoric*
- *ἀδιάβατος* = *adiabatos*  $\Rightarrow$  *impassable*  $\Rightarrow$  *adiabatic*
  - *ἀ~* = *a~*  $\Rightarrow$  *not*
  - *διάβατος* = *diabatos*  $\Rightarrow$  *passable*
  - *διά* = *dia*  $\Rightarrow$  *through*
  - *βαῖνειν* = *bainein*  $\Rightarrow$  *to walk, go, come*

## Born Square



**Faces** = thermodynamic potentials, adjacent to natural variables ( $\&N$ )

$$U = f\{S, V\} \quad H = f\{S, P\} \quad G = f\{T, P\} \quad F = f\{T, V\}$$

**Cross corners** = fundamental parameters/conjugate variables:  $(T, S)(P, V)(\mu, N)$

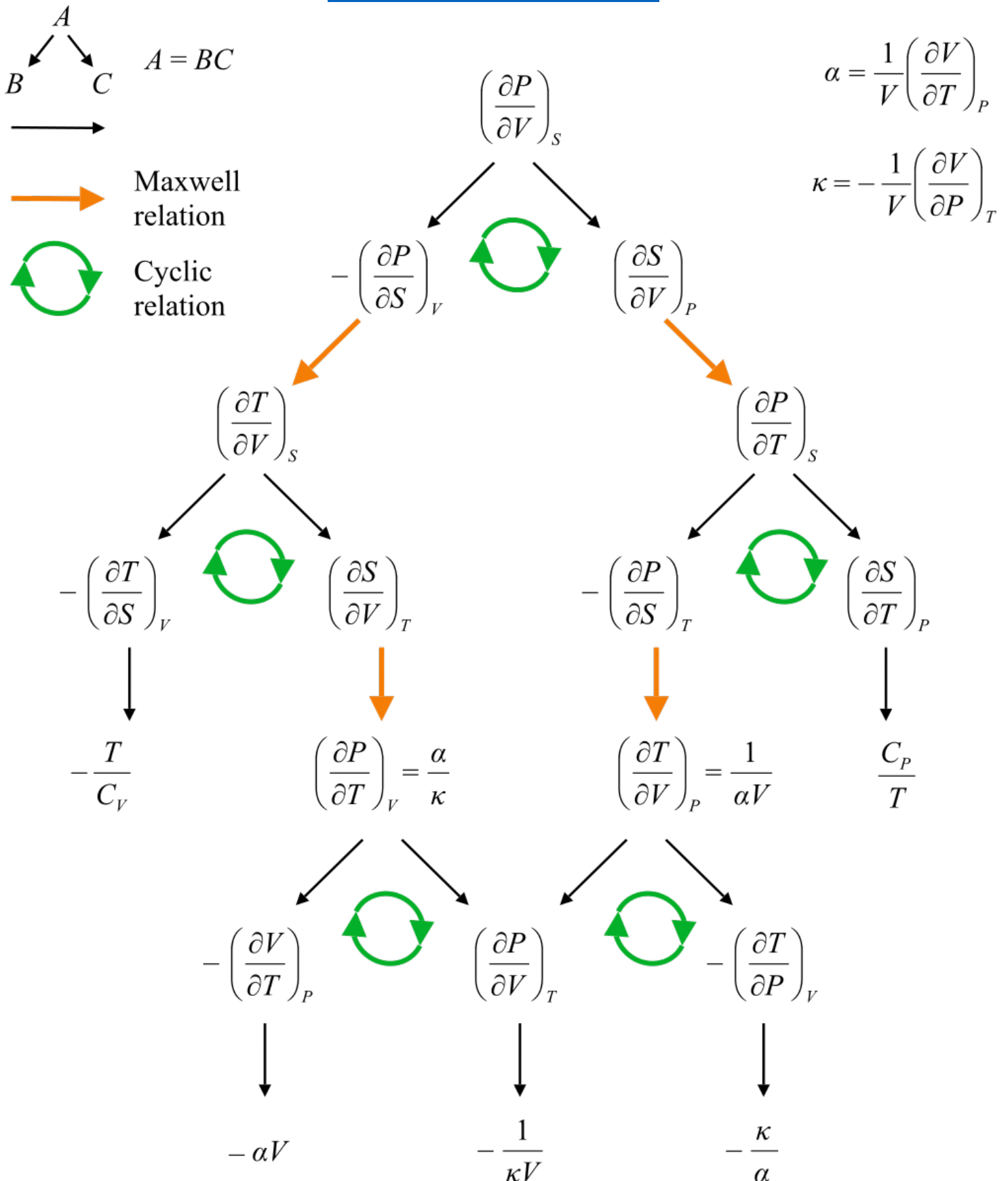
**U shapes** = Maxwell Relations ( $\Delta N = 0$ ), beware -'s includes constant var  
 Or differentiate potentials by natural variables ([Symmetry of 2nd Derivs](#))  
 Or use natural vars as denominator/constant, numerators = remaining, add negatives for  $U$  &  $G$

$$-\frac{d^2 F}{dTdV} = \left(\frac{dP}{dT}\right)_V = \left(\frac{dS}{dV}\right)_T \quad \dots \quad \left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P = \frac{d^2 G}{dTdP}$$

$$\frac{d^2 H}{dSdP} = \left(\frac{dV}{dS}\right)_P = \left(\frac{dT}{dP}\right)_S \quad \dots \quad \left(\frac{dT}{dV}\right)_S = -\left(\frac{dP}{dS}\right)_V = \frac{d^2 U}{dSdV}$$



# Maxwell Relations



\*Information in this document is compiled from Wikipedia, which is often doubted for itself being a compilation of sources. However, as a source of scientific information that is very well established like in Thermodynamics, I consider it a reliable source.