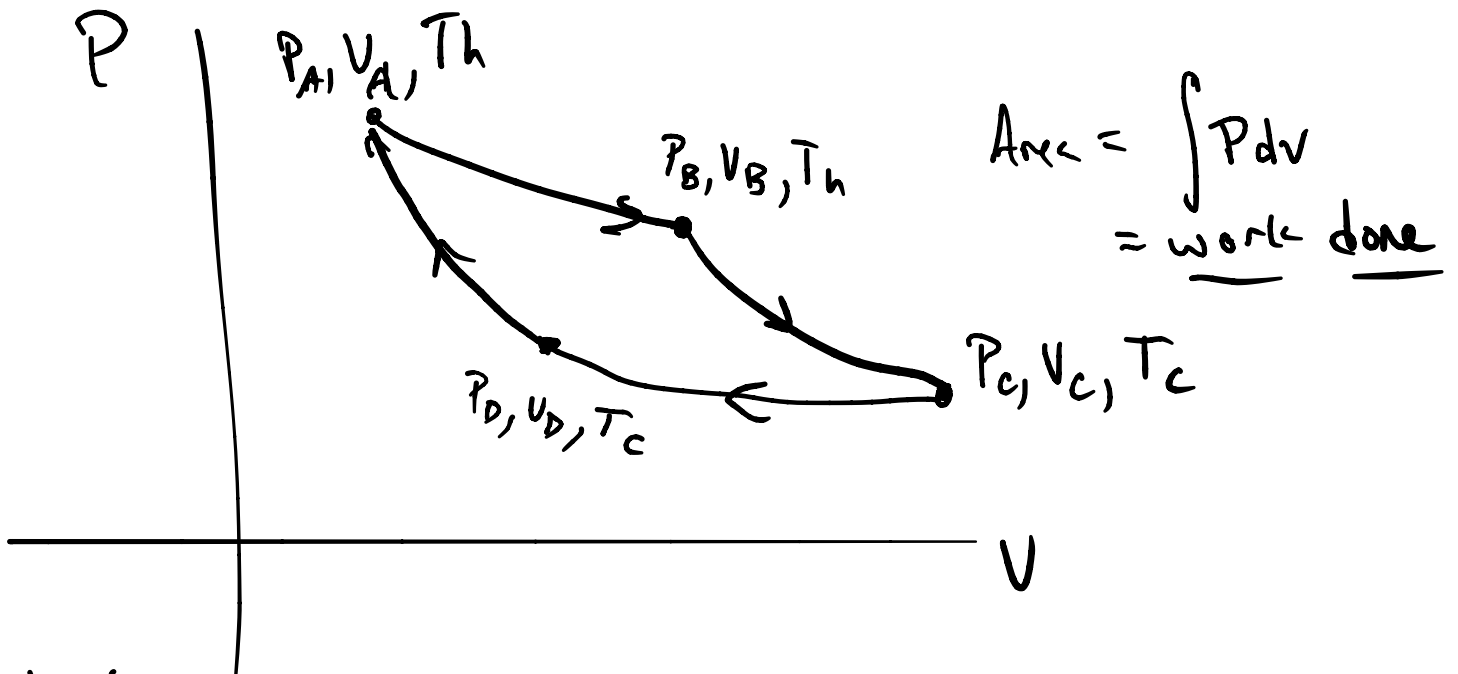Review of Carnot cycle from last time:
2 steps where system does work
$(w_{sys} < 0)$ and two where
the system has work done on it $(w_{sys} > 0)$

Isothermal — adiabatic — Isothermal — adiabatic
expansion   cooling   expansion   heating

P

P_A, V_A, T_h

P_B, V_B, T_h

$Area = \int P dv$
$= \underline{work\ done}$

P_C, V_C, T_C

P_D, V_D, T_C

V

Ideal gas:

Isothermal $\quad \Delta E = 0, \quad q = -w$

> 0

$w_{sys} = -\int_{v_1}^{v_2} P_{sys} dv = -\int_{v_1}^{v_2} \frac{nRT}{V} = -nRT \ln\left(\frac{v_2}{v_1}\right)$

$q = nRT \ln\left(\frac{v_2}{v_1}\right)$, $\quad$ heat in work out
$\qquad\qquad\qquad\qquad$ if expanding

Adiabatic $q = 0, \quad \Delta E = nc_v \Delta T = w$

cool: $T_c - T_h < 0 \Rightarrow w < 0$, does work

Column headers: q and w_{sys}

① isothermal expansion $\qquad q = q_{in}$ $\qquad nRT_h \ln(v_B/v_A)$ $\qquad -nRT_h \ln(v_B/v_A)$

② adiabatic expansion $\qquad 0 \qquad \Delta E = w = C_v(T_c - T_h)$

③ isothermal compression $\qquad nRT_c \ln(v_D/v_c) \qquad -nRT_c \ln(v_D/v_c)$

④ adiabatic compression $\qquad 0 \qquad w = +C_v(T_h - T_c)$

$$w_{total} = -nRT_h \ln(v_B/v_A) - nRT_c \ln(v_D/v_c)$$

$$w_{done} = -w_{total} = q_1 + q_3$$

$$\epsilon = \frac{-w}{q_{in}} = \frac{-w}{q_1} = \frac{q_1 + q_3}{q_1} = 1 + \frac{q_3}{q_1}$$

$$\frac{q_3}{q_1} = \frac{\cancel{nR}T_c \ln(v_D/v_c)}{\cancel{nR}T_h \ln(v_B/v_A)}$$

for adiabatic expansion, showed

$$v_f/v_i = \left(T_f/T_i\right)^{-C_v/nR} \implies \ln(v_D/v_c)/\ln(v_B/v_A)$$

$$= -1$$

$$\Rightarrow \boxed{\epsilon = 1 - T_c/T_h} \leftarrow \text{more general than ideal gas}$$

as $T_h \to \infty$, $\epsilon \to 1$

as $T_c \to 0$, $\epsilon \to 1$

Now $\dfrac{q_3}{q_1} = -\dfrac{T_c}{T_h} = -\dfrac{T_3}{T_1}$

$$\Rightarrow q_1/T_1 + \dfrac{q_3}{T_3} = 0$$

Suggests a quantity that is a state function, because any path around cycle adds up to zero

Can make many small carnot cycles add up

and take the limit
to small sizes

So $\sum_{cycle} q_i^{rev}/T = 0 \rightarrow \oint dq^{rev}/T = 0$

suggests we define $dS \equiv dq^{rev}/T$

State function & $\oint dS = 0$

$\Delta S = \int_i^f dS$ regardless of path ☆

Entropy for some reversible processes

1. Const P expansion

$\Delta S = \int_i^f \frac{dq^{rev}}{T} = \int_{T_1}^{T_2} c_p \frac{dT}{T}$

$dq = c_p dT$

$\xrightarrow{S_{1/2}R} = c_p \ln(T_2/T_1)$ if c_p const

ideal gas $= c_p \ln(v_2/v_1)$ b/c $v \propto T$

② Const volume

$$\Delta S = C_v \ln (T_2/T_1) \quad \text{for same reason}$$
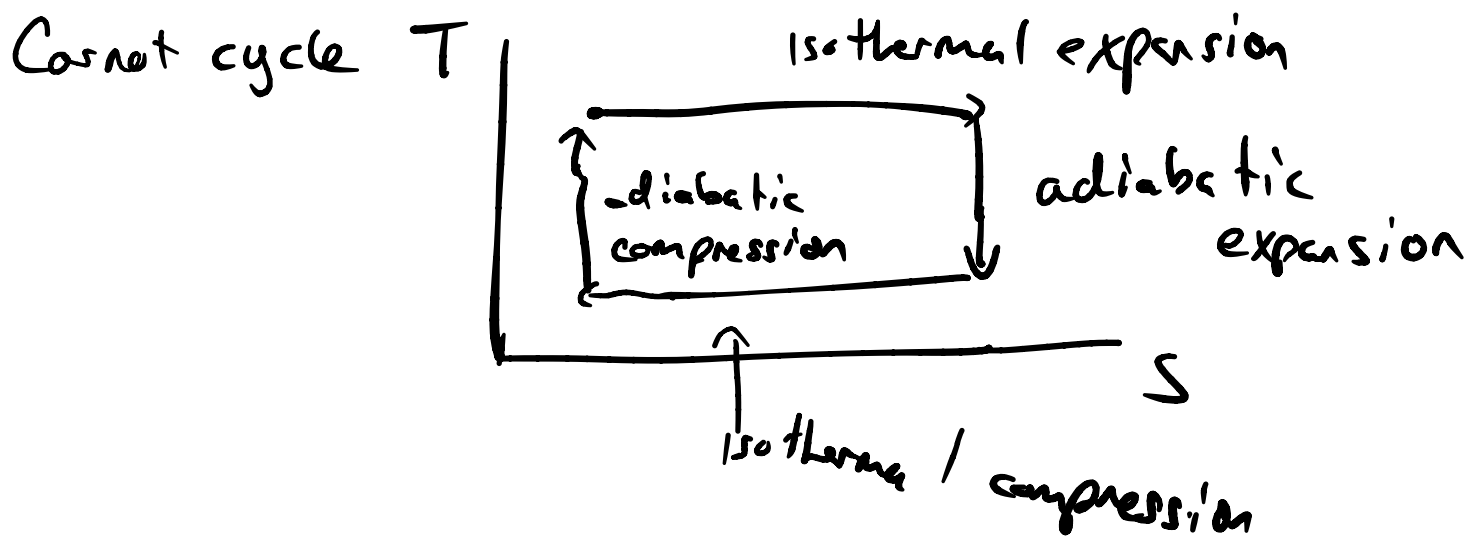$$= \frac{3}{2} R \ln (T_2/T_1) \quad \Leftarrow \text{mono ideal gas}$$

③ Const T, $d\varepsilon = 0$, $dq = -w = PdV$

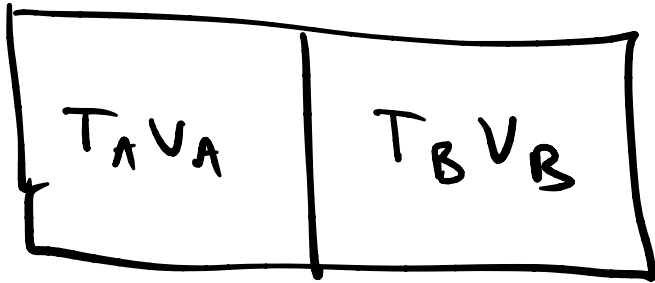$$\Delta S = \int_i^f \frac{dq^{rev}}{T} = \int_{V_1}^{V_2} \frac{P}{T} dV = nR \ln (V_2/V_1)$$

↖ ideal gas

in these two, have only T or V
because other is constant

④ adiabatic — $dq = 0 \Rightarrow \Delta S = 0$

Carnot cycle

T (vertical axis), S (horizontal axis)

Isothermal expansion
adiabatic compression
adiabatic expansion
Isothermal compression

Lets look at heat flow insted of cycles

Isolated
V_A fixed V_B fixed
heat flows until $T_L = T_R$

$\mathcal{E} = \mathcal{E}_A + \mathcal{E}_B$

$d\mathcal{E} = d\mathcal{E}_A + d\mathcal{E}_B$

$d\mathcal{E} = dq + dw$
$\underbrace{}_{0, \text{ const volume}}$

$dq^{rev} = TdS$

So $dS = dS_A + dS_B = \dfrac{d\mathcal{E}_A}{T_A} + \dfrac{d\mathcal{E}_B}{T_B}$

But here $d\mathcal{E}_A = -d\mathcal{E}_B$

$\Rightarrow dS = d\mathcal{E}_A \cdot \left(\dfrac{1}{T_A} - \dfrac{1}{T_B} \right)$

if $T_A > T_B$, $d\mathcal{E}_A < 0$

$\& \dfrac{1}{T_A} - \dfrac{1}{T_B} < 0$

Entropy increases!
Not conserved for closed sys.
In fact $= 0$ for equilibrium

and spontaneous processes occur
until entropy is <u>Maximized</u>

$dS > 0$ (spont process, isolated system)

$dS = 0$ (rev process isolated system)

For an irreversible process, <u>entropy</u>
<u>is</u> <u>produced</u> in the system

Now, if we are not in an isolated
system $\quad dS = dS_{prod} + dS_{exch}$

$$= dS_{prod} + đq/T$$

For reversible, $dS = đq^{rev}/T$

For irreversible, $dS_{prod} > 0$

$$\Rightarrow dS > đq^{irr}/T$$

$dS \geq đq/T$ any process $\left(\begin{array}{l}\text{equal for}\\ \text{rev}\end{array}\right)$

$\Delta S \geq \int đq/T \Leftarrow$ 2nd law eqn

Note, universe is closed system
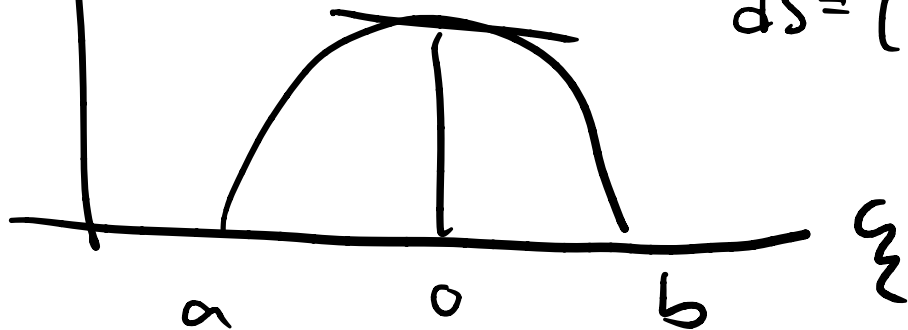so $dq = 0$ &
$dS > 0$ for any spontaneous
process!

Entropy as a thermodynamic potential
Suppose ξ says how far we are
from eq (like $[A] - [A_{eq}]$)

Then

$S(\xi) \Rightarrow$
$dS = \left(\frac{\partial S}{\partial \xi}\right) d\xi$

$\partial S / \partial \xi = 0$ @ eq,

$\partial S / \partial \xi > 0$ if $\xi < 0$

$dS / d\xi < 0$ if $\xi > 0$

Acts like a potential

Ex: heat flow btwn two bodies

$$T_f = \frac{T_A + T_B}{2}$$

Entropy is state func so although irreversible, can do const volume reversible cooling so

$$\Delta S_A = C_v \ln \left(T_f / T_A \right) \quad \text{(same substance)}$$

$$\Delta S_B = C_v \ln \left(T_f / T_B \right)$$

$$\Delta S = \Delta S_A + \Delta S_B$$

$$= C_V \ln \left(\frac{(T_A + T_B)^2}{4 T_A T_B} \right)$$

if $T_A = T_B = 0$

otherwise always positive

b/c $T_A^2 + 2 T_A T_B + T_B^2 - 4 T_A T_B$

$$= (T_A - T_B)^2 > 0 \quad \checkmark$$