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

Ideal gas:

Isothermal  \(\Delta E = 0\),  \(q = -w\)

\[w_{sys} = -\int_{V_1}^{V_2} P_{sys} \, dv = -\int_{V_1}^{V_2} \frac{NRT}{v} \, dv = -NRT \ln \left( \frac{V_2}{V_1} \right)\]

\[q = NRT \ln \left( \frac{V_2}{V_1} \right), \text{ heat in work out if expanding}\]

Adiabatic  \(q = 0\),  \(\Delta E = ncv \Delta T = w\)

cool:  \(T_c - T_h < 0 \Rightarrow w < 0\), does work
① Isothermal expansion
\[ \frac{q_1}{nRT_h \ln \left( \frac{V_B}{V_A} \right)} - nRT_h \ln \left( \frac{V_B}{V_A} \right) \]

② Adiabatic expansion
\[ 0 \quad \Delta E = w = C_v (T_c - T_h) \]

③ Isothermal compression
\[ nRT_c \ln \left( \frac{V_D}{V_c} \right) - nRT_c \ln \left( \frac{V_D}{V_c} \right) \]

④ Adiabatic compression
\[ 0 \quad \omega = + C_v (T_h - T_c) \]

\[ w_{\text{total}} = - nRT_h \ln \left( \frac{V_B}{V_A} \right) - nRT_c \ln \left( \frac{V_D}{V_c} \right) \]

\[ w_{\text{done}} = - w_{\text{total}} = q_1 + q_3 \]

\[ \epsilon = - \frac{w}{q_1} = - \frac{q_1 + q_3}{q_1} = 1 + \frac{q_3}{q_1} \]

\[ \frac{q_3}{q_1} = \frac{nRT_c \ln \left( \frac{V_D}{V_c} \right)}{nRT_h \ln \left( \frac{V_B}{V_A} \right)} \]

For adiabatic expansion, shumed

\[ \frac{V_f}{V_i} = \left( \frac{T_f}{T_i} \right)^{-C_v/nR} \Rightarrow \ln \left( \frac{V_D}{V_c} \right) / \ln \left( \frac{V_B}{V_A} \right) = -1 \]
\[ G = 1 - \frac{T_c}{T_h} \]

as \( T_h \to \infty \), \( G \to 1 \)
as \( T_c \to 0 \), \( G \to 1 \)

Now \( \frac{\Phi_3}{\Phi_1} = -\frac{T_c}{T_h} = -\frac{T_3}{T_1} \)

\[ \Rightarrow \frac{\Phi_1}{T_1} + \frac{\Phi_3}{T_3} = 0 \]

Suggests a quantity that is a
state function, because any path around cycle adds up to zero.
Can make many small cannot cycles add up and take the limit to small sites

\[ \sum \varphi_i^{\text{rev}} = 0 \rightarrow \oint \frac{dq^{\text{rev}}}{T} = 0 \]

cycle suggests we define \( dS = dq^{\text{rev}} / T \)

state function & \( \oint dS = 0 \)

\[ \Delta S = \int_{i}^{f} dS \] regardless of path

Entropy for some reversible processes

1. Const P expansion \[ \frac{V_f}{V_i} \]

\[ \Delta S = \int_{i}^{f} \frac{dq^{\text{rev}}}{T} = \int_{T_i}^{T_f} C_P dT \]

\[ dq = C_P dT \]

\[ S_{\text{ideal gas}} = C_P \ln \left( \frac{v_2}{v_1} \right) \text{ b/c } v_2 T \]
(2) Const volume
\[ \Delta S = C_v \ln \left( \frac{T_2}{T_1} \right) \] for some reason
\[ = \frac{3}{2} R \ln \left( \frac{T_2}{T_1} \right) \] more ideal gas

(3) Const \( T \), \( \text{d}E = 0 \), \( \text{d}q = -w = P \text{d}V \)
\[ \Delta S = \int_{V_1}^{V_2} \frac{P \text{d}V}{T} = \int_{V_1}^{V_2} \frac{nR \ln \left( \frac{V_2}{V_1} \right)}{T} \]
\[ \approx \text{ideal gas} \]

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

(4) adiabatic - \( \text{d}q = 0 \) \( \Rightarrow \) \( \Delta S = 0 \)
Cornet cycle \( T \)

\[ \begin{array}{c}
\text{isothermal expansion} \\
\text{adiabatic expansion} \\
\text{adiabatic compression} \\
\text{isothermal / compression}
\end{array} \]
Let's look at heat flow instead of cycles.

\[ T_{AV} \quad T_{BV} \]

(\text{isolated})

\[ V_A \text{ fixed } V_B \text{ fixed } \]

heat flows until \( T_L = T_R \)

\[ \begin{align*}
    E &= E_A + E_B \\
    dE &= dE_A + dE_B \\
    dq &= TdS
\end{align*} \]

\[ \begin{align*}
    dE &= dq + \frac{dE}{T} \\
    dE &= dq + \omega \frac{dE}{T}, \text{ const volume}
\end{align*} \]

So \( dS = dS_A + dS_B = dE_A / T_A + dE_B / T_B \)

But here \( dE_A = -dE_B \)

\[ \Rightarrow dS = dE_A \cdot \left( \frac{1}{T_A} - \frac{1}{T_B} \right) \]

If \( T_A > T_B \), \( dE_A < 0 \)

\[ \Rightarrow \frac{1}{T_A} - \frac{1}{T_B} < 0 \]

Entropy increases!

\[ \text{Not conserved for closed sys.} \]

In fact = 0 for equilibrium.
and spontaneous processes occur until entropy is maximized

\[ ds > 0 \] (spontaneous process, isolated system)

\[ ds = 0 \] (rev process isolated system)

For an irreversible process, entropy is produced in the system

Now, if we are not in an isolated system

\[ ds = dS_{\text{prod}} + dS_{\text{exch}} \]

\[ = dS_{\text{prod}} + \frac{dq_{\text{rev}}}{T} \]

For reversible, \( dS = \frac{dq_{\text{rev}}}{T} \)

For irreversible, \( dS_{\text{prod}} > 0 \)

\[ \Rightarrow ds > \frac{dq_{\text{rev}}}{T} \]

\[ ds \geq \frac{dq}{T} \] for any process (equal for rev)

\[ ds \geq \int \frac{dq}{T} \leq 2\text{nd law eqn} \]
Note, universe is closed system so $dq=0$ & $dS>0$ for any spontaneous process.

Entropy as a thermodynamic potential $\xi$ says how far are we from eq. (like $|A\xi-[A\xi]|$)

Then $S$

\[ S'(S)=\frac{3p}{\xi_0} \]

$S'_{\xi_0} = 0 \quad @ \quad eq.1 \quad S > 0 \quad if \quad \xi > 0$

$S'_{\xi_0} > 0 \quad if \quad \xi < 0$

Acts like a potential
**Ex:** heat flow between two bodies

\[ T_f = \frac{T_A + T_B}{2} \]

Entropy is a state function, so although irreversible, can do constant volume reversible cooling so

\[ \Delta S_A = C_v \ln \left( \frac{T_f}{T_A} \right) \quad \text{(same substance)} \]

\[ \Delta S_B = C_v \ln \left( \frac{T_f}{T_B} \right) \]

\[ \Delta S = \Delta S_A + \Delta S_B \]

\[ = C_v \ln \left( \frac{(2T_A + T_B)^2}{4T_A T_B} \right) \]

If \( T_A = T_B = 0 \)

otherwise always positive

\[ \because T_A^2 + 2T_A T_B + T_B^2 - 4T_A T_B \]

\[ = (T_A - T_B)^2 \geq 0 \]