Ch 1b Lecture 13
February 5th, 2012

Next few lectures – Still on the road to chemical reactivity, circa mid-1800s.

Today: Reversible processes, & Heat Engines
         (or, "Attack of the killer partial derivatives, part deux")

Reading: OGC Chapter 12, esp. section 12.6; & look ahead to Section 13.4 (Carnot Cycles)

02:12/02:   ⊟

Last time:

The First Law of Thermodynamics

$$\Delta U \ = \ q + w \ = nc_v \Delta T$$

The change in internal energy of a system is equal to the sum of the heat added to the system and the work done on the system. Although q and w depend *individually* on the path followed between a given pair of states, their **sum** does not.
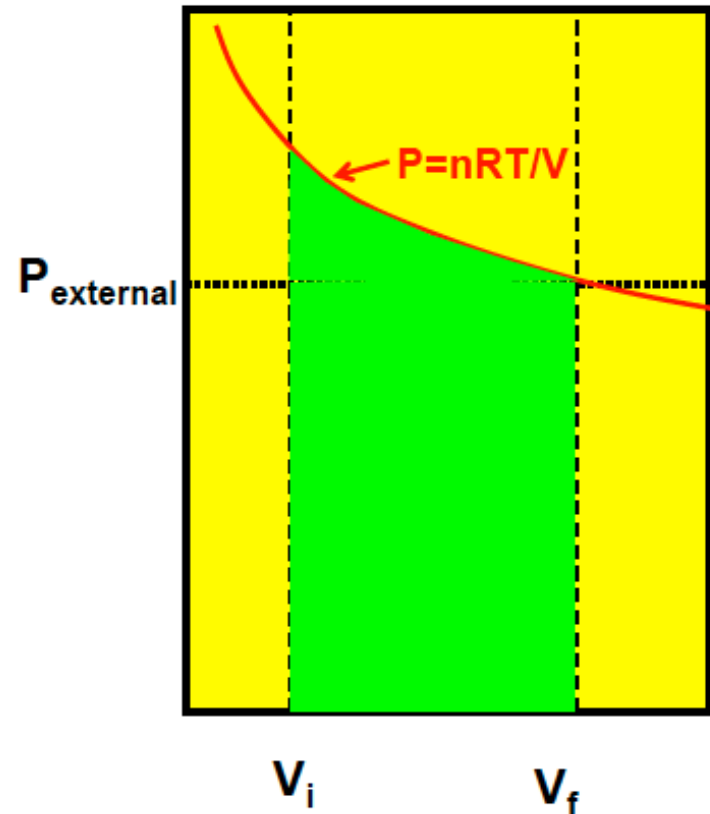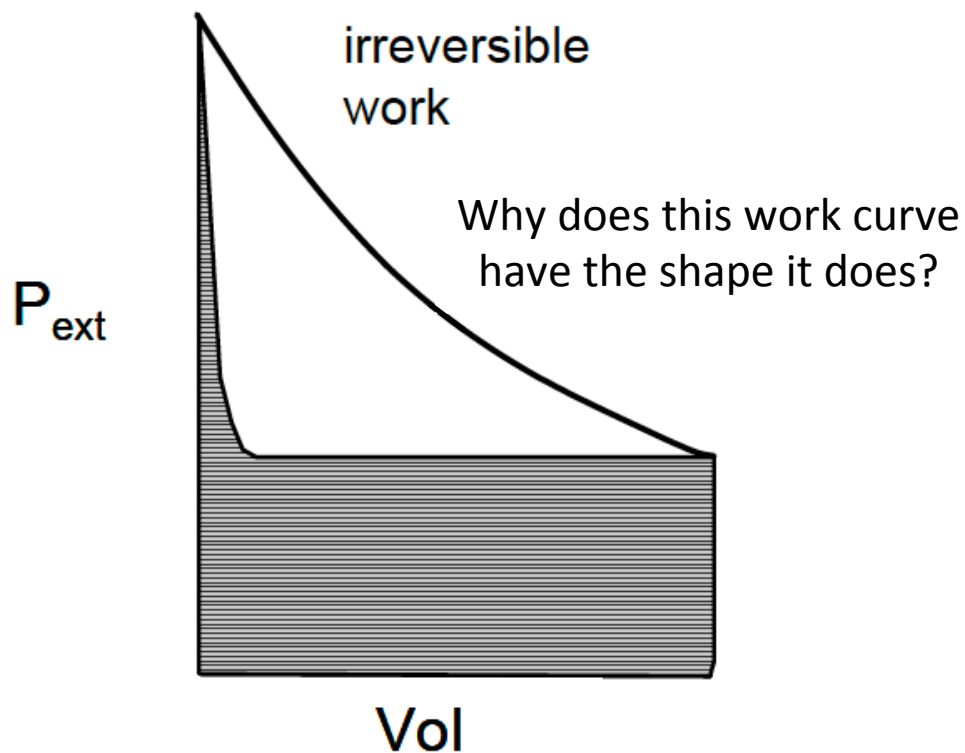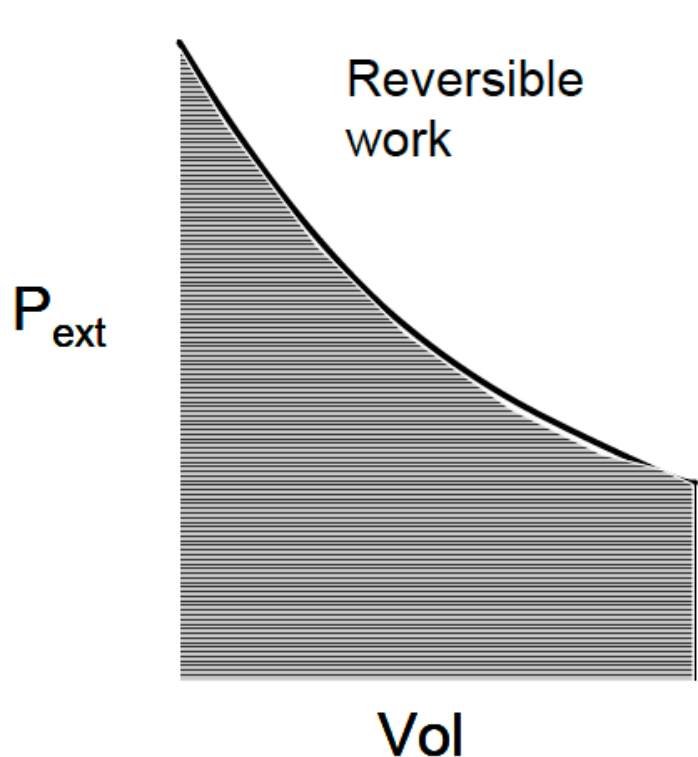
Enthalpy

$$\Delta H \ = \ \Delta U + \Delta(PV) = nc_p \Delta T$$

Work due to Gas Expansion:

The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm PV=nRT.

What do we mean by the term reversibly?

Reversible work

P_{ext}

Vol

irreversible work

Why does this work curve have the shape it does?

P_{ext}

Vol

Work done in a reversible process is always greater than work done in an irreversible process. In an irreversible expansion of a gas, for example, the volume and/or pressure is altered abruptly, rather than incrementally. However, the various state functions that describe the initial and final state are unchanged.

Thus, the work and heat flow in reversible & irreversible process should be different!

For both types of expansions:

n_i, V_i, P_i, and T_i are equal

n_f, V_f, P_f, and T_f are equal

But: work$_{rev}$ ≠ work$_{irrev}$

If the gas expanded against P_{ext}, then heat was put into the gas to get it to expand

Heat = q
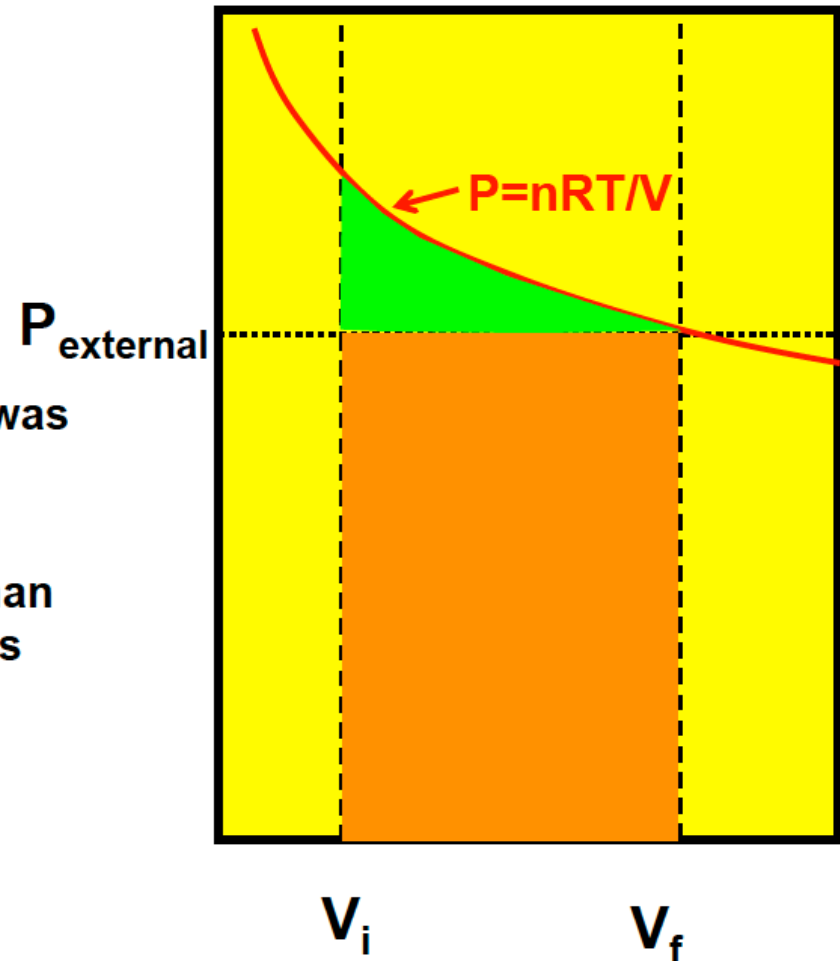
Reversible expansions are more efficient than irreversible expansions (hence more work is extracted)

$q_{rev} ≠ q_{irrev}$ (we will show this later)

N, V, P, and T are state functions

■ + ■ = reversible work
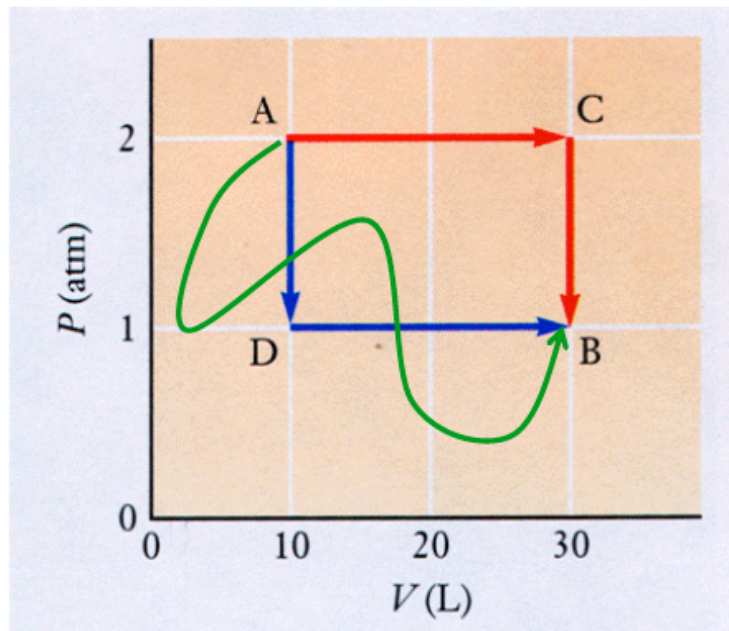
■ = irreversible work

P=nRT/V

$P_{external}$

V_i V_f

Are there "real life" reversible systems?

Last time, we looked at the following paths:

Other Pathways

How about the green path?

Why?
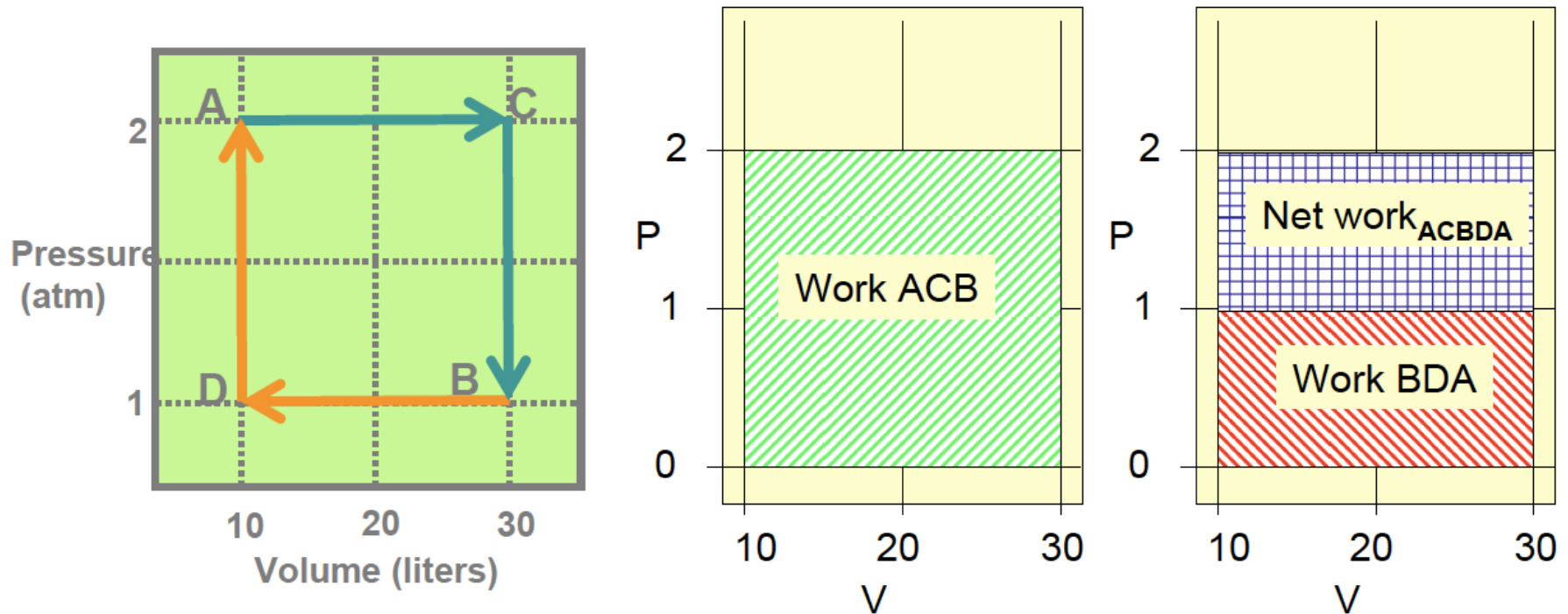Because **ΔU is a state function** – it is pathway independent

$$\Delta U_{Green} = q + w = 15 l \cdot atm = 1520 J$$

Path	q	w	q+w
ACB	5570 J	-4050 J	1520 J
ADB	3550 J	-2030 J	1520 J

= all pathways A→B

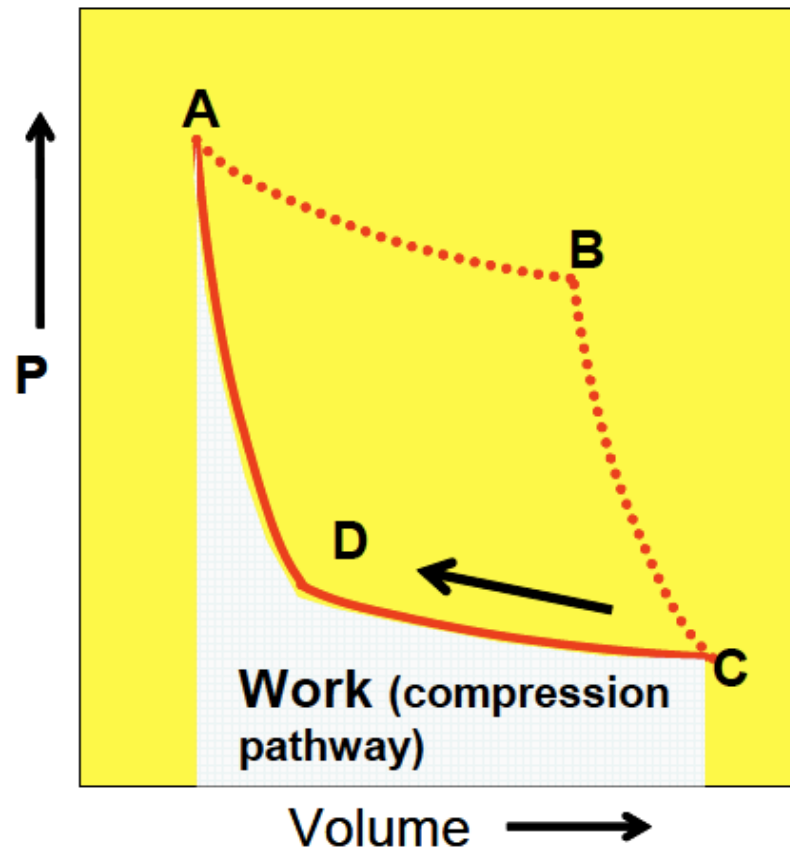Calculating *q, w*?
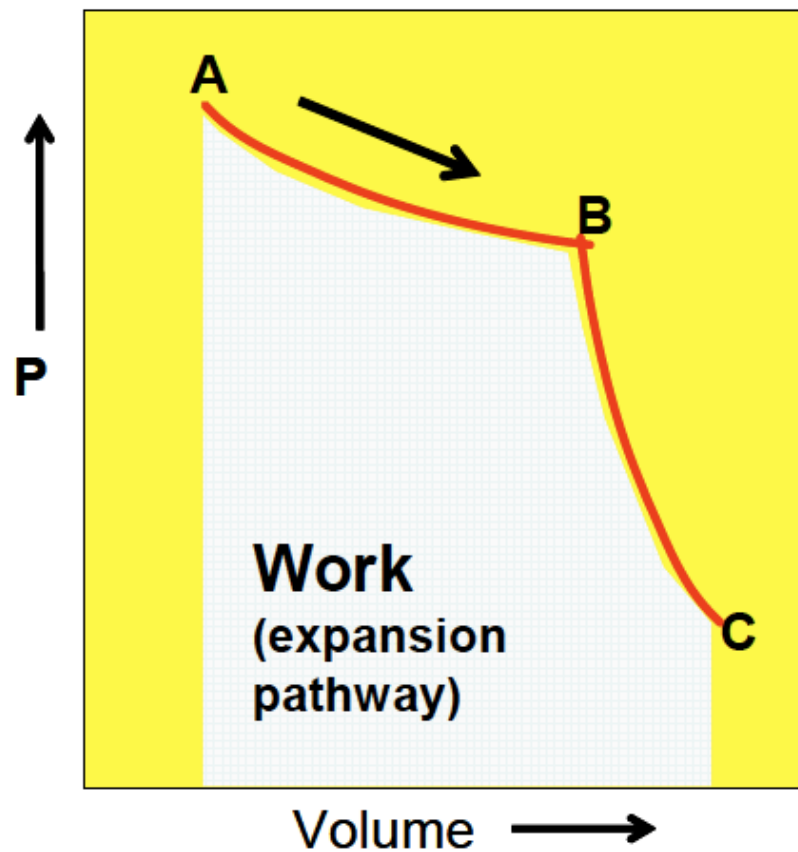
What is the efficiency of this cycle?

$$\text{Efficiency} = \text{work}_{net}/q_{in}$$

While $q_{in} + q_{out}$ might equal net heat, the q_{out} is wasted heat (we don't get it back), and so we only count the q_{in}

We will show in a bit that the maximum efficiency of this cycle is only 10-20%.

Extracting Work from a System

Two different pathways between A and C. The work for each pathway is represented by the shaded area. Note that if we compress the system along ABC, and expand along the CDA, the net result is that we can get a good yield of work out of the system.

Extracting Work from a System
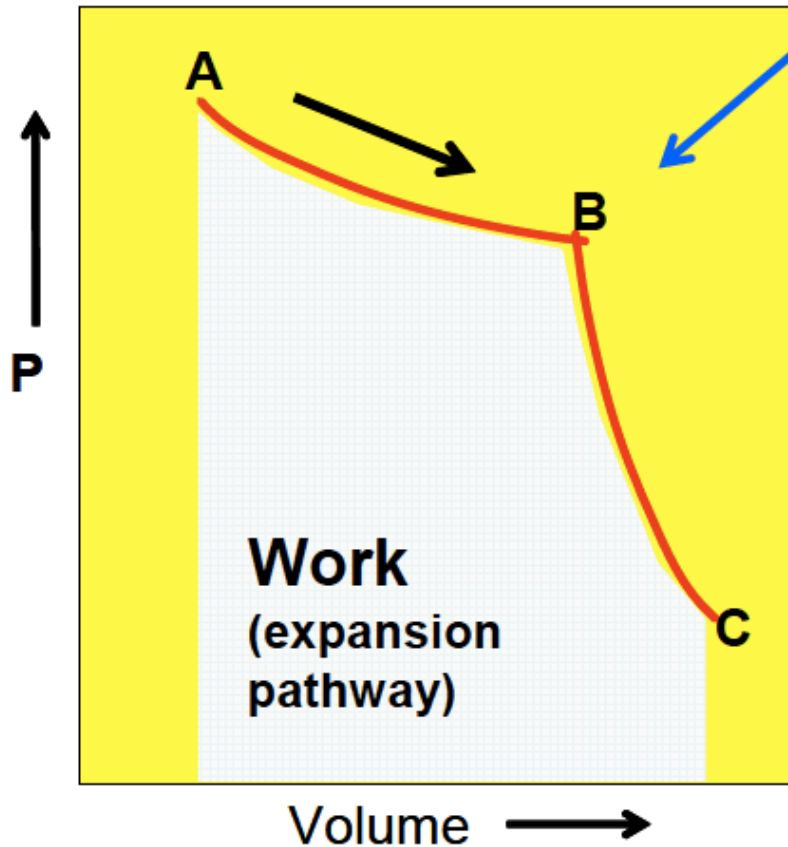
Assume the graph describes the cycle of an engine

We expand a piston so that it travels from A→C;

We compress the piston so that it returns from C→A;

What pathways can we construct so that we maximize the work out of the system?

Here, we will consider the maximum thermodynamic efficiency of a *reversible* cycle (so we can move forward or back); and to do this we'll need to examine **isothermal** (constant T) and **adiabatic** (no heat exchange) legs.

Isothermal Processes

P$_{ext}$ changes as volume changes in
an isothermal, reversible expansion
of an ideal gas
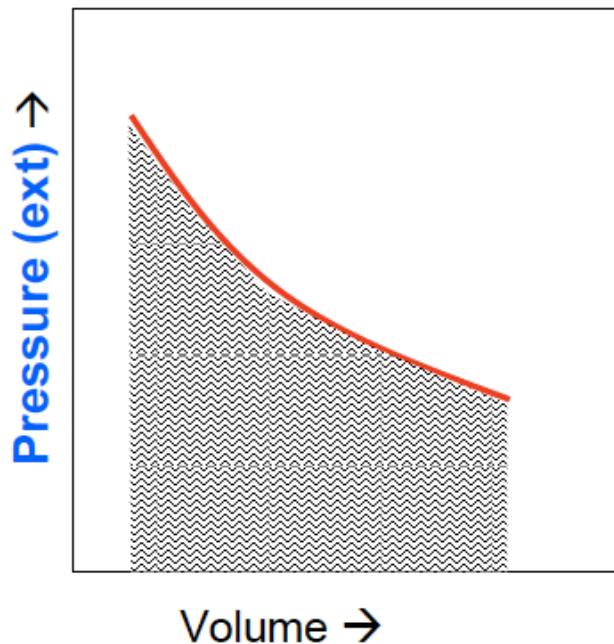
For an isothermal processes
$\Delta T = 0$ so $\Delta U = nc_V\Delta T = 0 = q + w$

$$\Delta U = q + w = 0$$

So:

$$q = -w$$

Isothermal Processes

For an isothermal processes
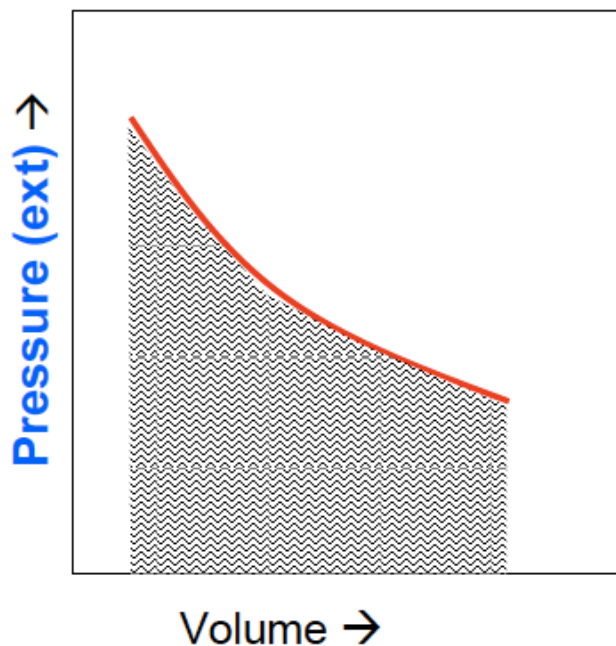$\Delta T = 0$ so $\Delta U = nc_V\Delta T = 0 = q + w$
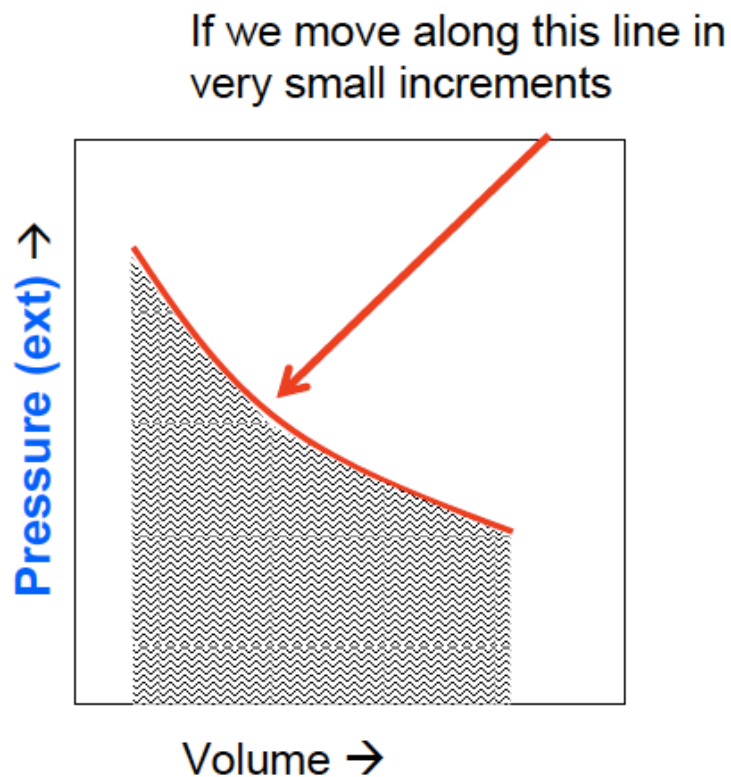

$$\Delta U = q + w = 0$$

So:

$$w = -q$$

$$w \neq -P_{ext}\Delta V$$

thus

$$P_{ext} = \frac{nRT}{V}$$

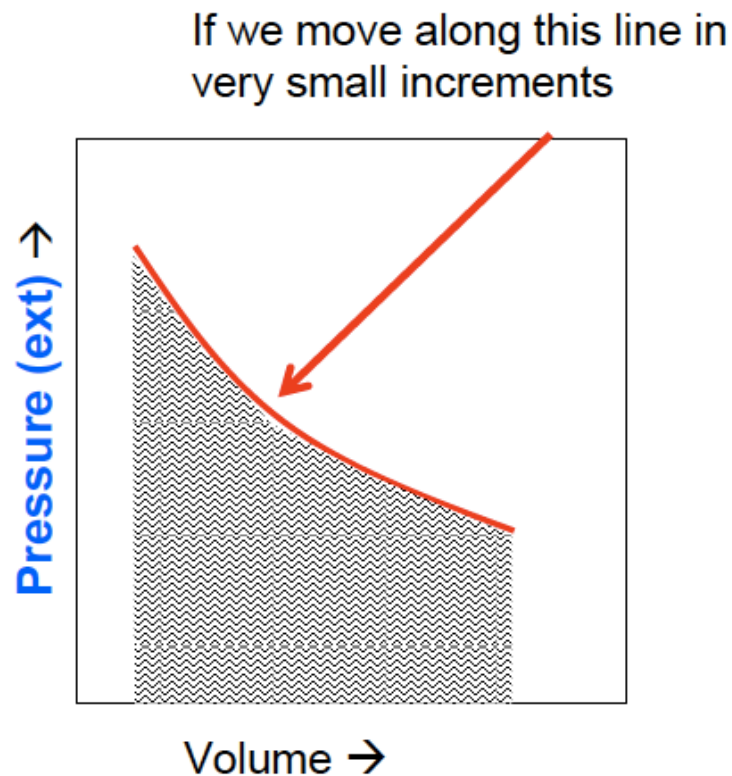# Isothermal Processes

If we move along this line in very small increments

Pressure (ext) →

Volume →

$$P_{ext} = \frac{nRT}{V}$$

$$w = -\int_{V_1}^{V_2} P\,dV$$

$$w = -nRT\int_{V_1}^{V_2} \frac{1}{V}\,dV = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

Isothermal Processes

If we move along this line in
very small increments

Pressure (ext) →

Volume →

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -q$$

Note that since $\Delta T = 0$
$\Delta H \, (=\Delta U + \Delta(nRT)) = 0$

Adiabatic Processes

An adiabatic system cannot exchange heat with it's surroundings, so Δq=0.

ΔU = work = w

Recall that:

$$dU = nc_V dT = w \quad \text{For a small change}$$

$$nc_V dT = -PdV = \frac{-nRT}{V}dV$$

Adiabatic Processes

An adiabatic system cannot exchange heat with it's surroundings, so $\Delta q=0$.

$\Delta U = \text{work} = w$

Recall that:

$$dU = nc_V dT = w \quad \text{For a small change}$$

$$nc_V dT = -P dV = \frac{-nRT}{V} dV$$

Divide through by nT

$$\frac{c_V dT}{T} = \frac{-R}{V} dV$$

Adiabatic Processes

An adiabatic system cannot exchange heat with it's surroundings, so $\Delta q = 0$.

$\Delta U = \text{work} = w$

$$\frac{c_V dT}{T} = \frac{-R}{V} dV$$

$$c_V \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{V_2}{V_1}\right) = R \ln\left(\frac{V_1}{V_2}\right)$$

Adiabatic Processes

An adiabatic system cannot exchange heat with it's surroundings, so $\Delta q = 0$.

$\Delta U = \text{work} = w$

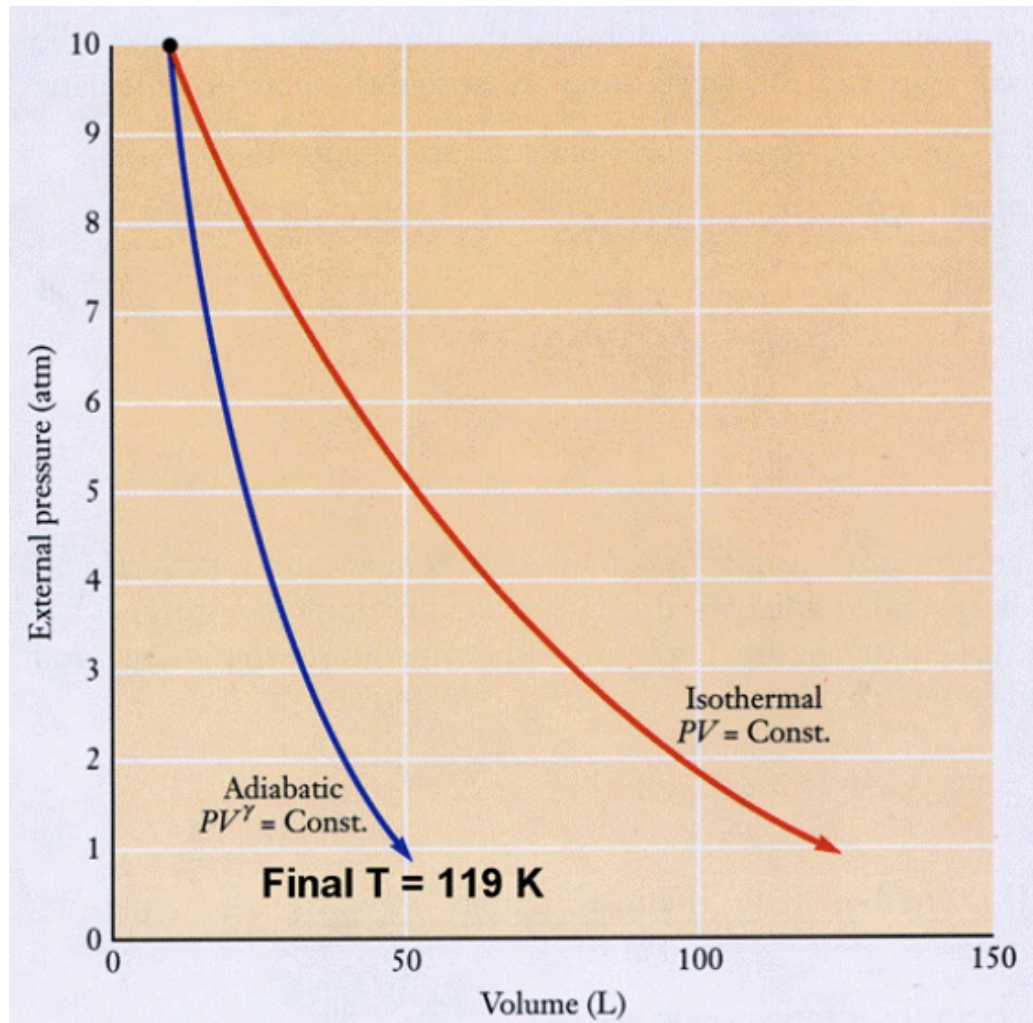$$c_V \ln\left(\frac{T_2}{T_1}\right) = R \ln\left(\frac{V_1}{V_2}\right)$$

Since $c_V = 3/2R$ and $c_P = 5/2R$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

where

$$\gamma = \frac{c_P}{c_V} = \frac{5}{3}$$

Isothermal versus Adiabatic Processes

Thus, we see that isothermal and adiabatic expansions (or compressions) with take different paths through (P,V) space and will arrive at different final states from the same initial state.

How different?

Isothermal versus Adiabatic Processes

$Temp_{initial}$ = 300K

$Volume_{initial}$ = 3 liters $Volume_{final}$ = 10 liters

$Pressure_{initial}$ = 3 atmospheres

Assume that this is an ideal gas

We can solve for $n_{initial}$ by solving

3 atm x 3 liters = **n** (0.082 liters atm mol^{-1} K^{-1}) 300 K

$n_{initial}$ **=0.37 moles**

Recall that
$$\gamma = \frac{c_P}{c_V} = \frac{5}{3}$$

And that
$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$
Holds for an adiabatic process

Isothermal versus Adiabatic Processes

$Temp_{initial} = 300K$ $n_{initial} = 0.37$ moles
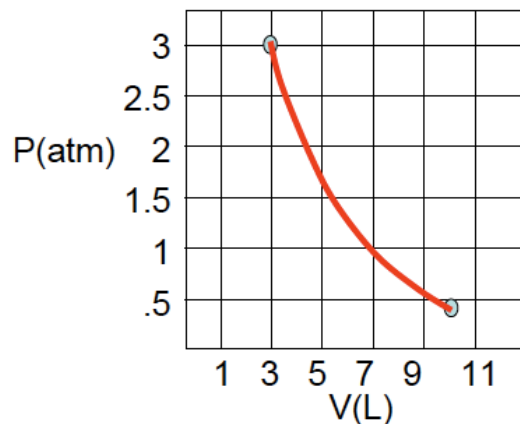
$Volume_{initial} = 3$ liters $Volume_{final} = 10$ liters

$Pressure_{initial} = 3$ atmospheres

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{T_2}{300}\right) = \left(\frac{3}{10}\right)^{2/3}$$

$$P_2V_2 = nRT_2; \quad P_2 = 0.403atm$$

$T_2 = 134$ K

Isothermal versus Adiabatic Processes

$\text{Temp}_{initial}$ = 300K $n_{initial}$ = 0.37 moles
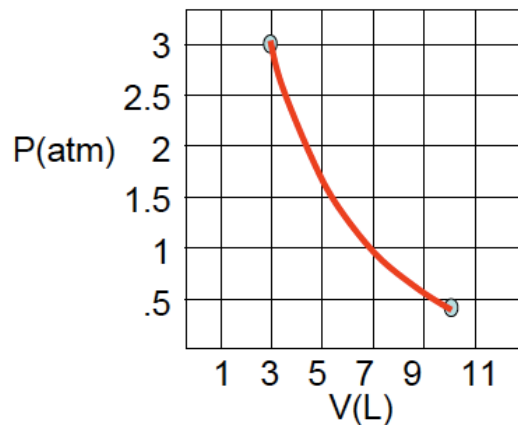
$\text{Volume}_{initial}$ = 3 liters Volume_{final} = 10 liters

$\text{Pressure}_{initial}$ = 3 atmospheres

$$P_2V_2 = nRT_2; \boxed{P_2 = 0.403atm} \qquad T_2 = 134\ K$$

Since q=0,
$\Delta U = w$ = 0.37(134-300)R = -770 J

And, since $\Delta H = \gamma \Delta U$
$\Delta H = 5\Delta U/3$ = -1284 J

Isothermal versus Adiabatic Processes

$Temp_{initial}$ = 300K $n_{initial}$ = 0.37 moles
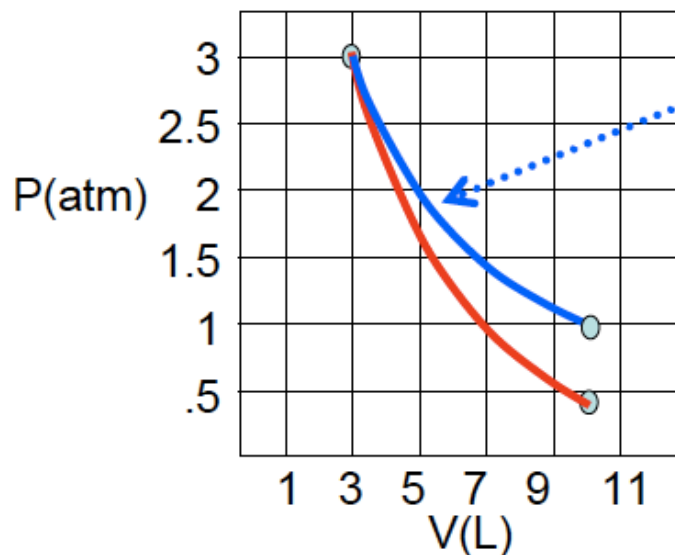
$Volume_{initial}$ = 3 liters $Volume_{final}$ = 10 liters

$Pressure_{initial}$ = 3 atmospheres P_f = ?

Same exact system, but we move from $V_i \rightarrow V_f$ <u>isothermally</u>

T_{final} = 300 K = T_i

Isothermal versus Adiabatic Processes

$Temp_{initial}$ = 300K $n_{initial}$ = 0.37 moles

$Volume_{initial}$ = 3 liters $Volume_{final}$ = 10 liters

$Pressure_{initial}$ = 3 atmospheres P_f = ?

Same exact system, but we move from $V_i \rightarrow V_f$ __isothermally__

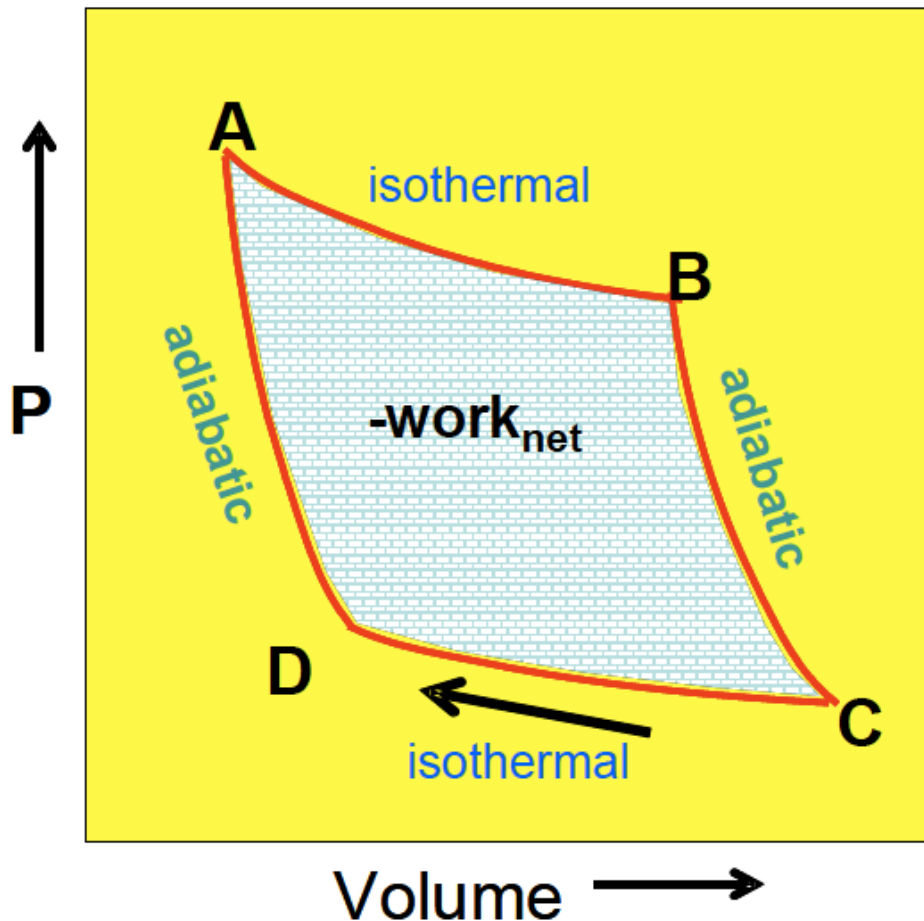$$ w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -q $$

$$ = -(0.37 moles)(8.314 J \cdot mol^{-1} K^{-1} \cdot 300K)\left(\ln \frac{10}{3}\right) $$
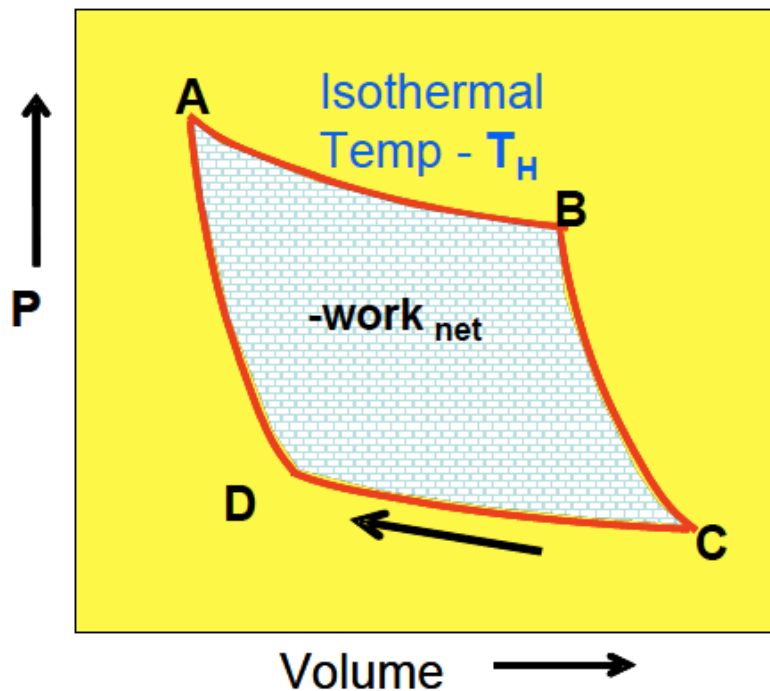
$$ = -1111 J $$

ΔU, ΔH ?

OK, now we can tackle the Carnot Cycle

Efficiency = $work_{out}/q_{in}$

We need to calculate how much work we can get out of this system for a given amount of heat input

How efficient can this engine be?
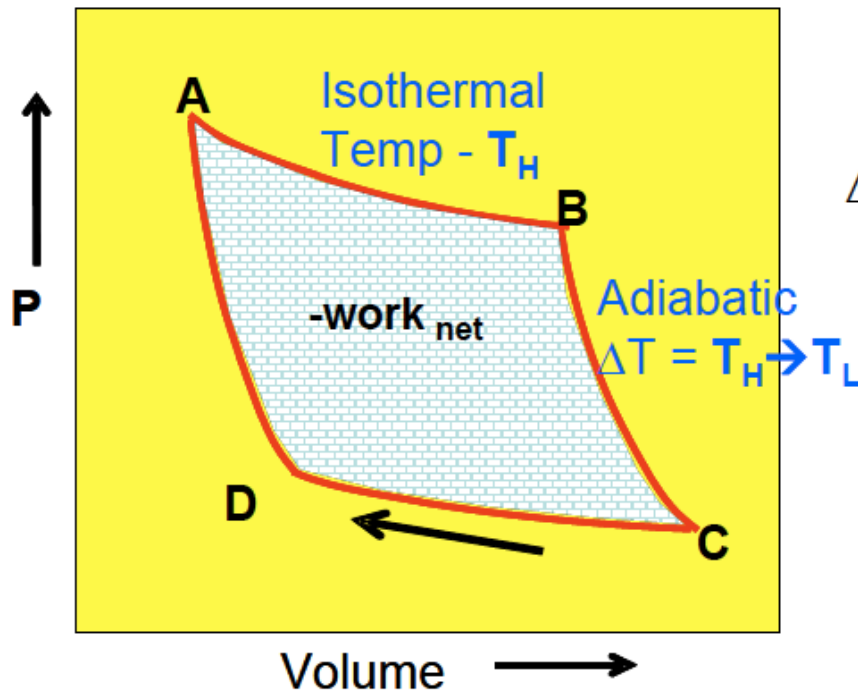
OK, now we can tackle the Carnot Cycle

How efficient?

A→B

$$w_{AB} = -q_{AB} = -nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

OK, now we can tackle the Carnot Cycle
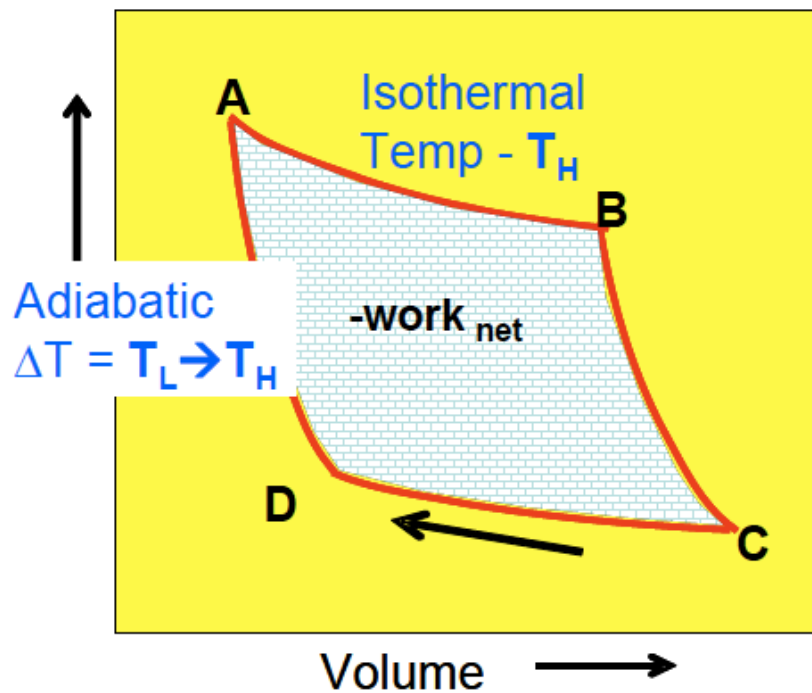
Work out the various pathways first

B→C

$$\Delta U_{BC} = w_{BC} = nc_V\left(T_L - T_H\right)$$

q=0

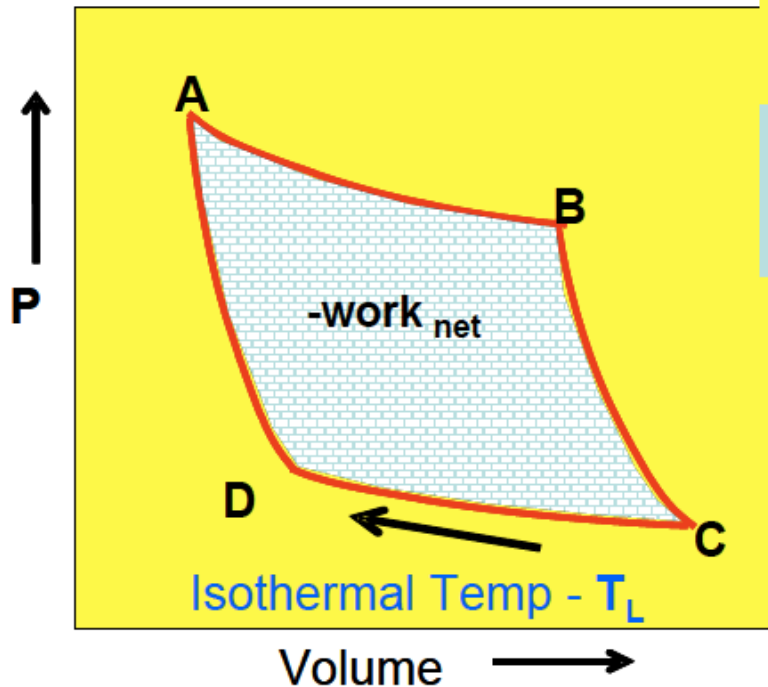# OK, now we can tackle the Carnot Cycle

Work out the various pathways first

Skipping to D→A   q=0

$$\Delta U_{DA} = \boxed{w_{DA}} = nc_V (T_H - T_L)$$

A

Isothermal
Temp - T_H

B

Adiabatic
$\Delta T = T_L \rightarrow T_H$

-work $_{net}$

D

C

Note that this exactly cancels out $\boxed{w_{BC}}$

Volume

$$\Delta U_{BC} = \boxed{w_{BC}} = -nc_V (T_L - T_H) = \boxed{-w_{DA}}$$

OK, now we can tackle the Carnot Cycle

Since $w_{BC} = -w_{DA}$, all work is along pathways A→B and C→D

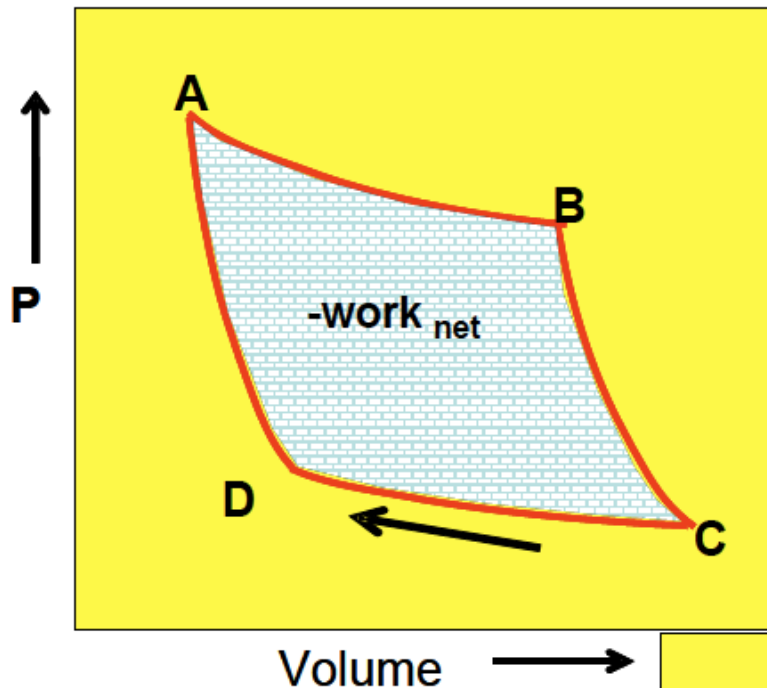Thus, $w_{BC} + w_{DA} = 0$

i.e. all work is along pathways A→B and C→D

pathway C→D

$$w_{CD} = -q_{CD} = -nRT_L \ln\left(\frac{V_D}{V_C}\right)$$

OK, now we can tackle the Carnot Cycle

How efficient?

$$w_{AB} = -q_{AB} = -nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$w_{CD} = -q_{CD} = -nRT_L \ln\left(\frac{V_D}{V_C}\right)$$

$w_{total} = -\text{work}_{net}$

$$w_{total} = -nRT_H \ln\left(\frac{V_B}{V_A}\right) + nRT_L \ln\left(\frac{V_C}{V_D}\right)$$

Why don't we worry about $w_{BC} + w_{DA}$ contributions?

OK, now we can tackle the Carnot Cycle

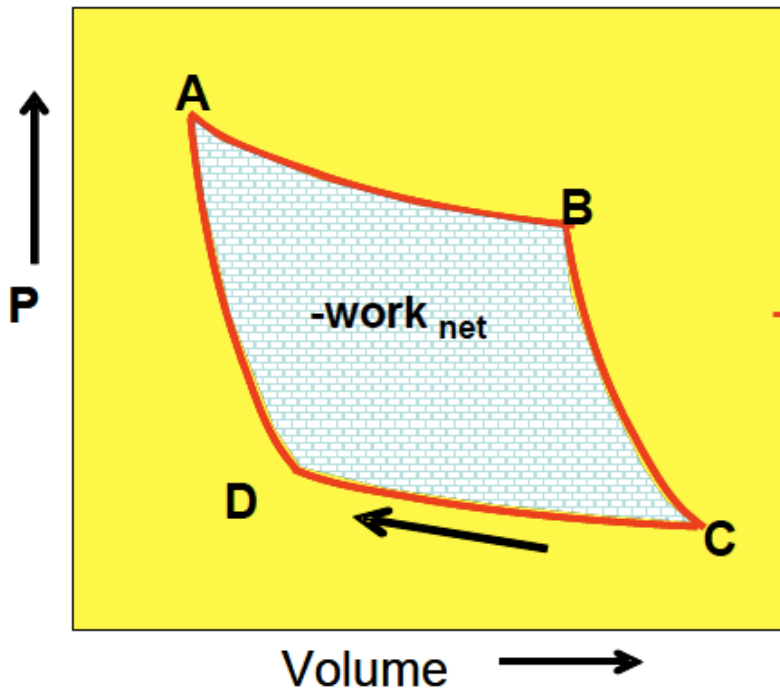$$w_{AB} - w_{CD} = w_{total}$$

How efficient?

$$w_{total} = -nRT_H \ln\left(\frac{V_B}{V_A}\right) + nRT_L \ln\left(\frac{V_C}{V_D}\right)$$

Recall that, for an adiabatic process

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Thus we can set up the following equalities

$$\left(\frac{T_H}{T_L}\right) = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \quad and \quad \left(\frac{T_H}{T_L}\right) = \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

P

A

B

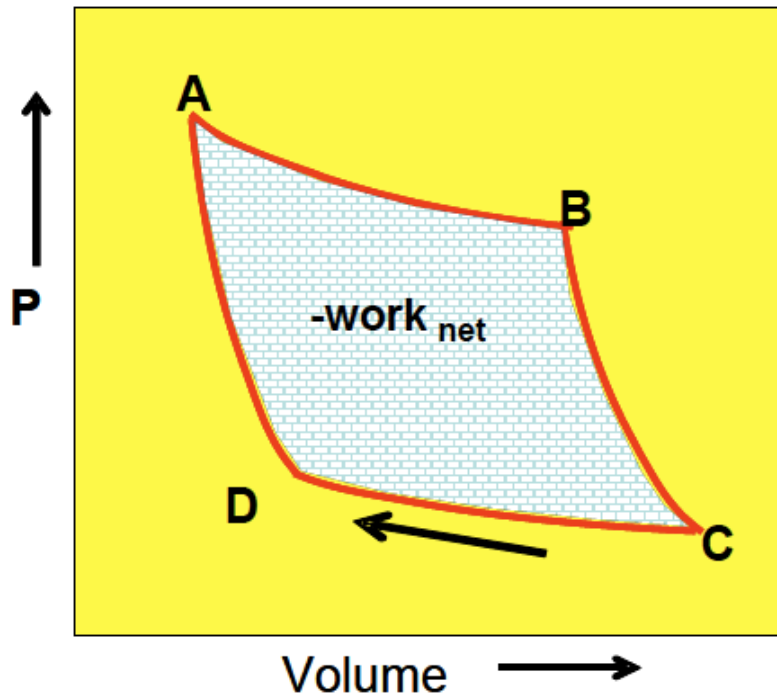-work $_{net}$

D

C

Volume

OK, now we can tackle the Carnot Cycle

$$w_{AB} - w_{CD} = w_{total}$$

How efficient?

$$w_{total} = -nRT_H \ln\left(\frac{V_B}{V_A}\right) + nRT_L \ln\left(\frac{V_C}{V_D}\right)$$

-work net

P

Volume

$$\left(\frac{T_H}{T_L}\right) = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \quad and \quad \left(\frac{T_H}{T_L}\right) = \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

So that $$\left(\frac{V_C}{V_D}\right) = \left(\frac{V_B}{V_A}\right)$$

$$w_{total} = -nR(T_H - T_L)\ln\left(\frac{V_B}{V_A}\right)$$

(that is, the system does work)
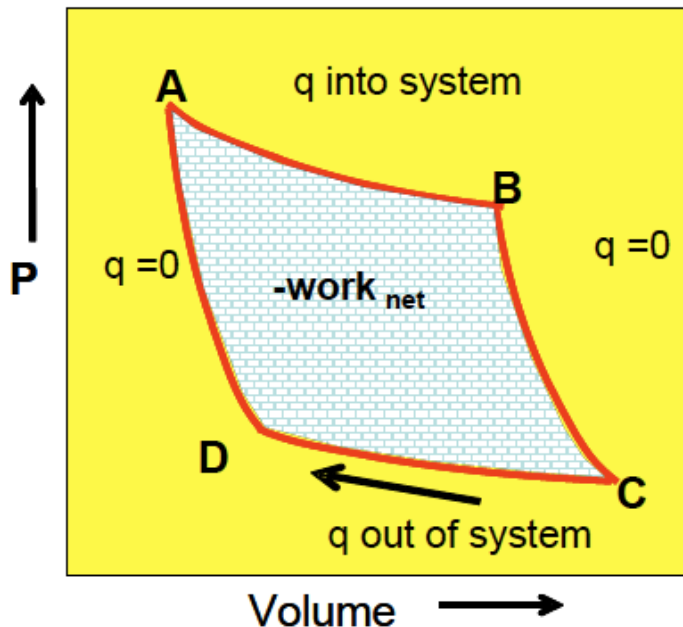
OK, now we can tackle the Carnot Cycle

Now we can calculate the efficiency of the Carnot engine

$$eff = \frac{-w_{net}}{|q_{AB}|}$$

$$w_{total} = -nR(T_H - T_L)\ln\left(\frac{V_B}{V_A}\right)$$

$$w_{AB} = -q_{AB} = -nRT_H \ln\left(\frac{V_B}{V_A}\right)$$
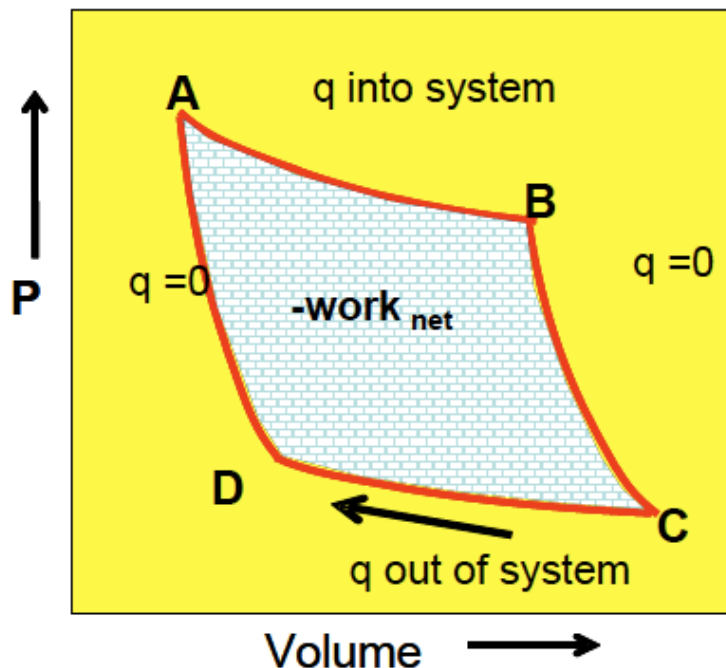
$$eff = \frac{-w_{net}}{|q_{AB}|} = \frac{nR(T_H - T_L)\ln\left(\frac{V_B}{V_A}\right)}{nRT_H \ln\left(\frac{V_B}{V_A}\right)}$$

A — q into system
B
q =0 — q =0
P
-work net
D
C
q out of system
Volume

OK, now we can tackle the Carnot Cycle

Now we can calculate the efficiency of the Carnot engine
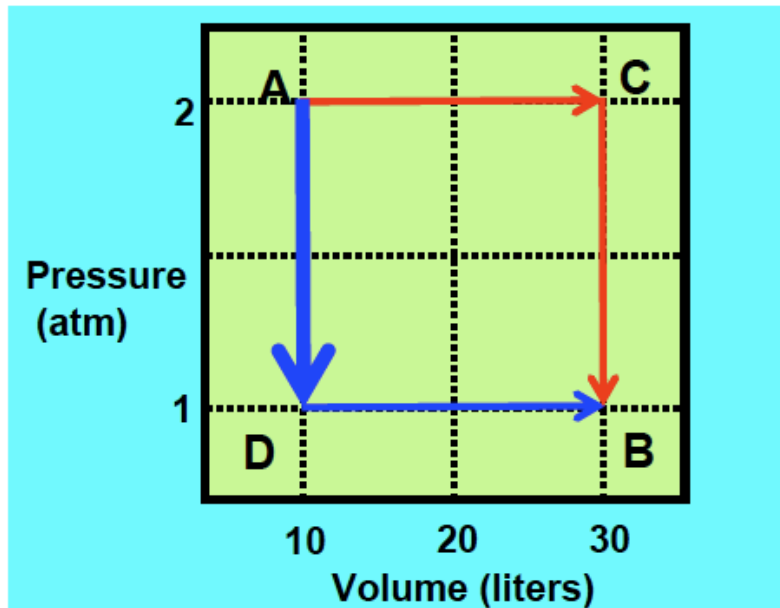
$$eff = \frac{-w_{net}}{|q_{AB}|} = \frac{n\cancel{R}(T_H - T_L)\ln\left(\cancel{\frac{V_B}{V_A}}\right)}{n\cancel{R}T_H\ln\left(\cancel{\frac{V_B}{V_A}}\right)}$$

q into system

A

B

q =0   q =0

P

-work net
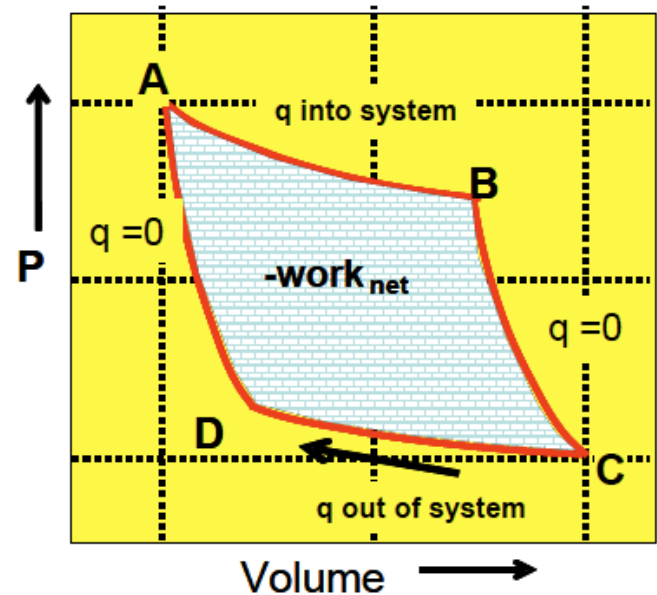
D

C

q out of system

Volume

$$eff = \frac{-w_{net}}{|q_{AB}|} = 1 - \frac{T_L}{T_H}$$

An elegantly simple solution!

Reversible & Irreversible Efficiencies: Example

Calculate efficiency of irreversible process first

$w_{A-C} = -2(30-10) = -40$ liter·atm $q_{A-C} = nc_p\Delta T; = 5/2nR\Delta T = 5/2\Delta(PV) = 5/2 (60-20) = 100$ liter-atm

$w_{C-B} = 0$ $q_{C-B} = nc_v\Delta T; = 3/2nR\Delta T = 3/2\Delta PV = 3/2(30-60) = -45$ liter atm

$w_{B-D} = -1(10-30) = 20$ liter·atm;

$q_{B-D} = nc_p\Delta T = 5/2nRDT = 5/2 D(PV) = 5/2 (10-30) = -50$ liter atm

$w_{D-A} = 0$

$q_{D-A} = nc_v\Delta T = 3/2nRDT = 3/2 D(PV) = 3/2(20-10) = 15$ liter atm

Reversible & Irreversible Efficiencies: Example
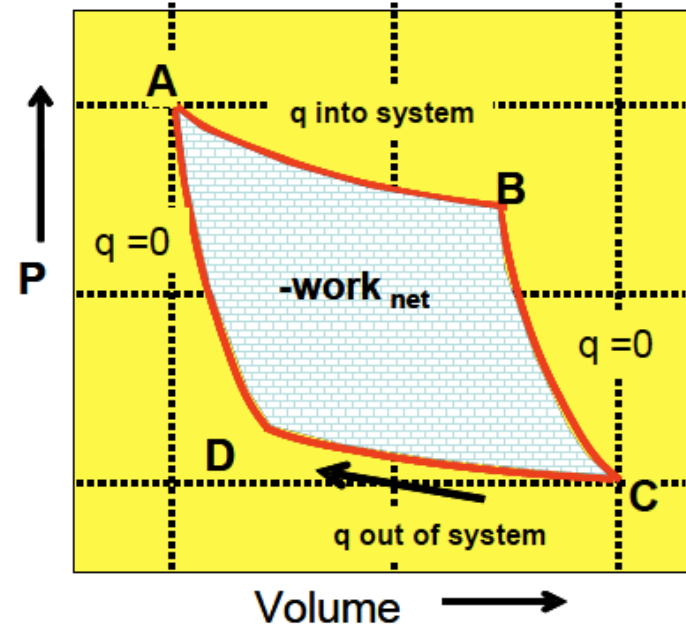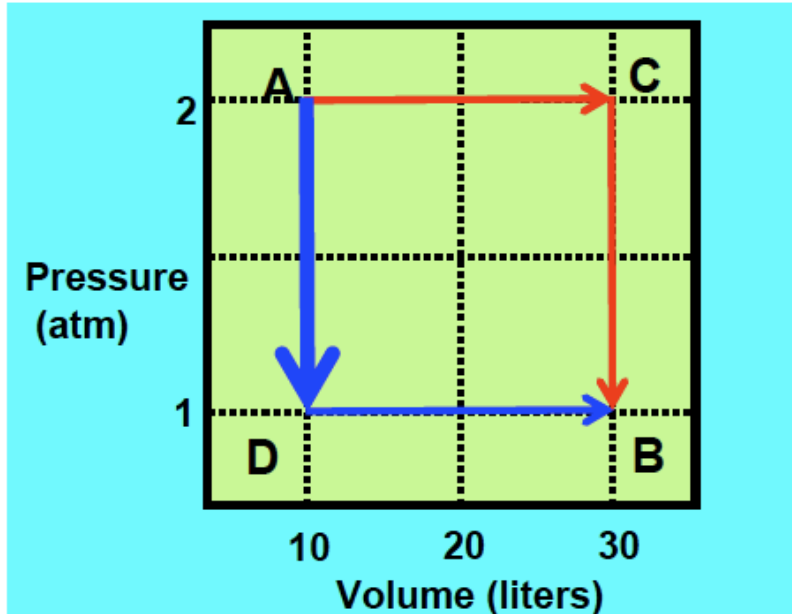
Work total = w_{A-C} + w_{C-B} + w_{B-D} + w_{D-A} = -40 liter·atm + 20 liter·atm = -20 liter·atm.

Heat total = q_{A-C} + q_{C-B} + q_{B-D} + q_{D-A} = q_{in} + q_{out}
= 100 liter·atm - 45 liter·atm -50 liter·atm + 15 liter·atm
= 115 liter·atm   –   95 liter·atm .

Heat in   Heat out (wasted)

Efficiency = work$_{out}$ / q$_{in}$ = -20 liter atm / 115 liter atm = 17.4%

Reversible & Irreversible Efficiencies: Example
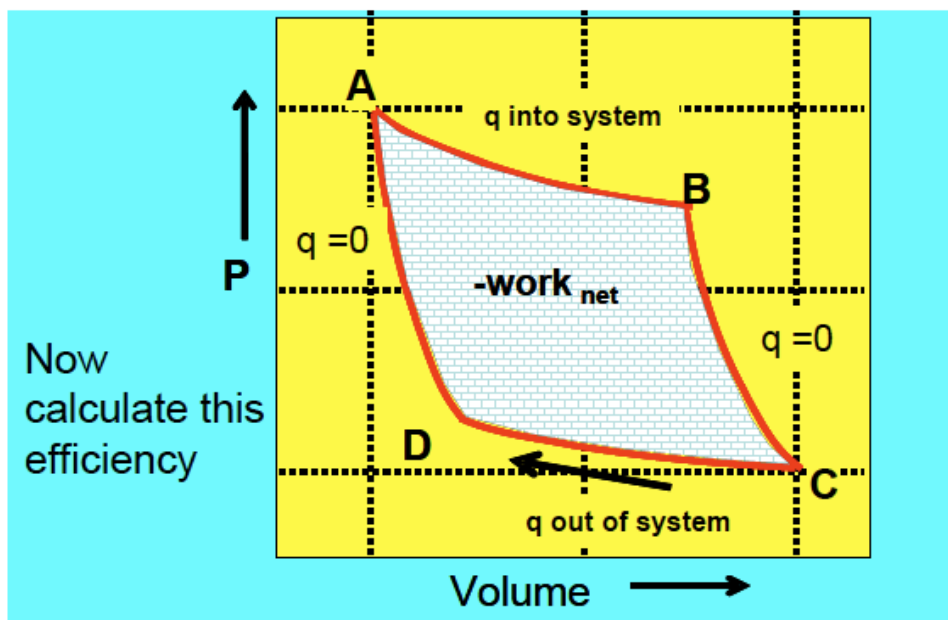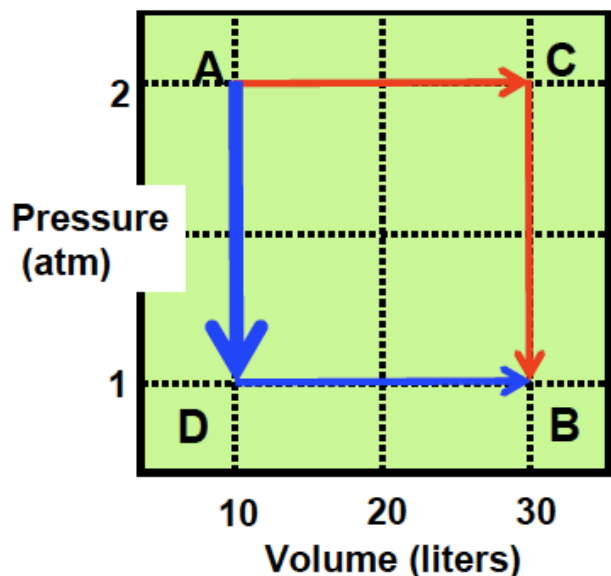
Assume at A: n = 0.81 moles; P_A = 2 atm; V_A = 10 liters; T_A = 300K
We expand A→B (isothermal) from 10 to 30 liters

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -q$$

w=-22 liter atm
q = 22 liter atm

P_B = (0.81 moles·0.0821 liter·atm·mol⁻¹·K⁻¹·300 K)/(30 liters) = 0.66 atm

B→ C (adiabatic) : n = 0.81 moles; P_B = .66 atm; V_B = 30 liters; T_B = 300K
We expand B→C so so that V_C=100 liters. Calculate ΔT, work, ΔU, etc.
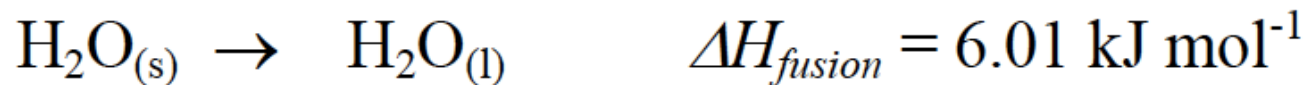
$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\frac{T_L}{300K} = (30/100)^{2/3}$$

T_L= 134 K

$$eff = \frac{-w_{net}}{|q_{AB}|} = 1 - \frac{T_L}{T_H}$$

=55%

Thermochemistry & Engines

Enthalpies and phase changes

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \qquad \Delta H_{fusion} = 6.01 \text{ kJ mol}^{-1}$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H_{vap} = 40.7 \text{ kJ mol}^{-1}$$

How much energy to:

10 g ice at 0°C → 10 g steam at 100°C

10 g/ 18 g mol^{-1} = 0.556 moles

$$\Delta H = \Delta H^0_{fusion} + \Delta H^0_{\Delta water} + \Delta H^0_{vaporization}$$

Specific heat of water

Thermochemistry & Engines
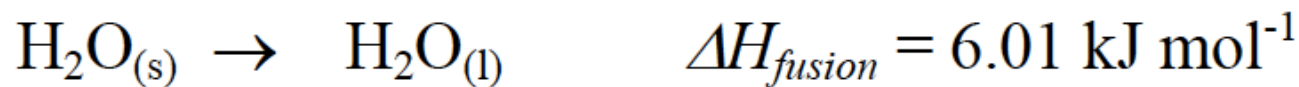
Enthalpies and phase changes

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \qquad \Delta H_{fusion} = 6.01 \text{ kJ mol}^{-1}$$

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H_{vap} = 40.7 \text{ kJ mol}^{-1}$$

How much energy to:

10 g ice at 0°C → 10 g steam at 100°C

10 g/ 18 g mol^{-1} = 0.556 moles

$$\Delta H = \Delta H^0_{fusion} + \Delta H^0_{\Delta water} + \Delta H^0_{vaporization}$$

$$\Delta H = \Delta H^0_{fusion}\left(= 0.556 M \times 6.01 kJ \cdot mol^{-1}\right)$$

$$+ \Delta H^0_{\Delta water}\left(= 4.184 J \cdot K^{-1} \cdot g^{-1} \times 10 g \times 100 K\right)$$

$$\Delta H^0_{vaporization}\left(= 0.556 mol \times 40.7 kJ \cdot mol^{-1}\right) = 30.15 kJ$$

Thermochemistry & Engines

$$\Delta H = \Delta H^0_{fusion} \left(= 0.556 M \times 6.01 kJ \cdot mol^{-1} \right)$$

$$+ \Delta H^0_{\Delta water} (= 4.184 J \cdot K^{-1} \cdot g^{-1} \times 10g)$$

$$\Delta H^0_{vaporization} \left(= 0.556 mol \times 40.7 kJ \cdot mol^{-1} \right) = 30.18 kJ$$

Work from this process → generate 10 g steam at 100°C

$$W = -P(V_2 - V_1) = \Delta nRT \qquad \Delta n = \text{# moles water vapor generated}$$

$$W = -1 atm(V_2 - 0.01L) = 0.556 mol \times 0.082 L \cdot atm \cdot mol^{-1} \cdot K^{-1} \times 373K$$

~17 **L·atm** of work, or -1.7kJ

Thermochemistry & Engines

$$\Delta H = \Delta H^0_{fusion} \left(= 0.556M \times 6.01kJ \cdot mol^{-1} \right)$$

$$+ \Delta H^0_{\Delta water} \left(= 4.184J \cdot K^{-1} \cdot g^{-1} \times 10g \right)$$

$$\Delta H^0_{vaporization} \left(= 0.556mol \times 40.7kJ \cdot mol^{-1} \right) = \boxed{30.18kJ}$$

22.6 kJ for converting boiling water to steam

Work generated from this process → produce 10 g steam at 100°C from 10 g water at room T (298K)

$$W = -1atm(V_2 - 0.01L) = 0.556mol \times 0.082L \cdot atm \cdot mol^{-1} \cdot K^{-1} \times 373K$$

~17 **L·atm** of work, or **-1.7kJ**

-1.7kJ/**30.18kJ** = 5.6% efficiency

Not very efficient!

Thermochemistry & Engines

$$\Delta H = \Delta H^0_{fusion}\left(= 0.556M \times 6.01 kJ \cdot mol^{-1}\right)$$

$$+ \Delta H^0_{\Delta water}(= 4.184 J \cdot K^{-1} \cdot g^{-1} \times 10g)$$

$$\Delta H^0_{vaporization}\left(= 0.556 mol \times 40.7 kJ \cdot mol^{-1}\right) = 30.18 kJ$$

30.1 kJ for converting room temp water to steam

Work generated from this process → produce 10 g steam at 100°C

-1.7kJ/30.1kJ = 5.6% efficiency

Steam engines were not efficient – especially when one considers that the wood or coal was often incompletely burned and that much of the heat from the burning was lost – the efficiencies were << 6.6%

Best we can do if all processes are reversible:

Carnot Efficiency: $1 - T_L/T_H$ = (1 – 298/373) = 20%
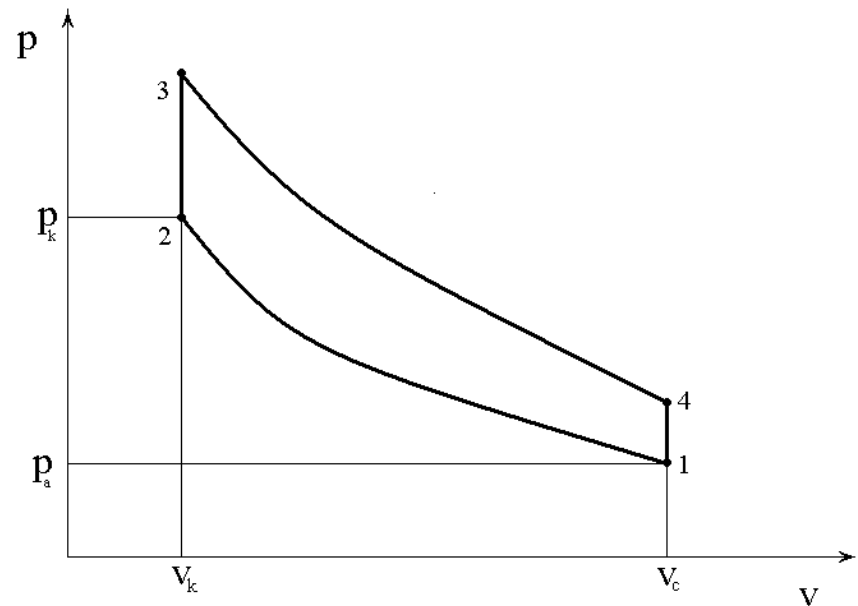
Thermochemistry & Engines
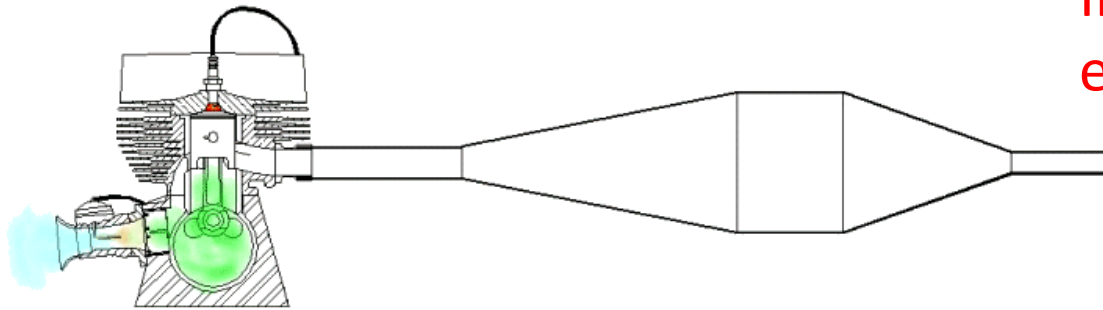
Internal Combustion engines do rather better.

Thermodynamic limit?

Typically about 35-37% (rocket engines can be as high as 70%, why?)

Average efficiencies are more like 20%, for a well designed engine & drive train. MPG depends on vehicle, driver…

Otto Cycle in PV Space (Four Stroke Engine)