Lecture 3: State Functions

- Reading: Zumdahl 9.3, 9.4
- Outline
  - Example of Thermo. Pathways
  - State Functions
  - (9.4…for laboratory)
- Problems: (Z9.72,Z9.84),(Z9.29,Z9.30),(Z9.32,Z9.38)
- Z9.13 (Find the mistake)

Summary:

All Systems

$$\Delta E = q + w$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$w = -P\Delta V + w_{other}$$

Ideal Monatomic Gas

- $C_v = 3/2R$
- $C_p = C_v + R = 5/2\ R$

Polyatomic Gas

- $C_v > 3/2R$
- $C_p > 5/2\ R$
- $C_P = C_V + R$

Ideal Gas

$$\Delta E = nC_v\Delta T \overset{\Delta V=0}{=} q_V$$

$$\Delta H = nC_p\Delta T \overset{\Delta P=0}{=} q_P$$

$$C_P = C_V + R$$

$$If\ \Delta T = 0,\ then\ \Delta E = 0$$

$$and\ q = -w$$

Meaning of State Functions

- Any function that can be written as a function of P,V and/or T (with n fixed) is a state function.
- q and w <u>cannot</u> be written in terms of the state of the system.
- Equation of State gets rid of one variable.
- e.g. I.G.E: $PV = nRT$ ties P, V and T (and n) together.
- Intensive properties: P and T, concentrations
- Molar anything (like molar heat capacities, molar energy etc.)
- Extensive properties: V, n, all energies and entropy.
- Example:
  - Write the I.G.E. in terms of intensive properties only.
  - Show that E for the I.G. is a function of P, V and/or T.

Thermodynamic Pathways: an Example

For a function that depends only on the state: The change in that function between states must be independent of the path between the two states.

- Example 9.2. We take 2.00 mol of an ideal monatomic gas and undergo the following change:
  - Initial (State A): $P_A = 2.00$ atm, $V_A = 10.0$ L
  - Final (State B): $P_B = 1.00$ atm, $V_B = 30.0$ L
    - We'll do this two ways:

      Path 1: Expand then Reduce Pressure

      Path 2: Reduce Pressure then Expand

Thermodynamic Jargon

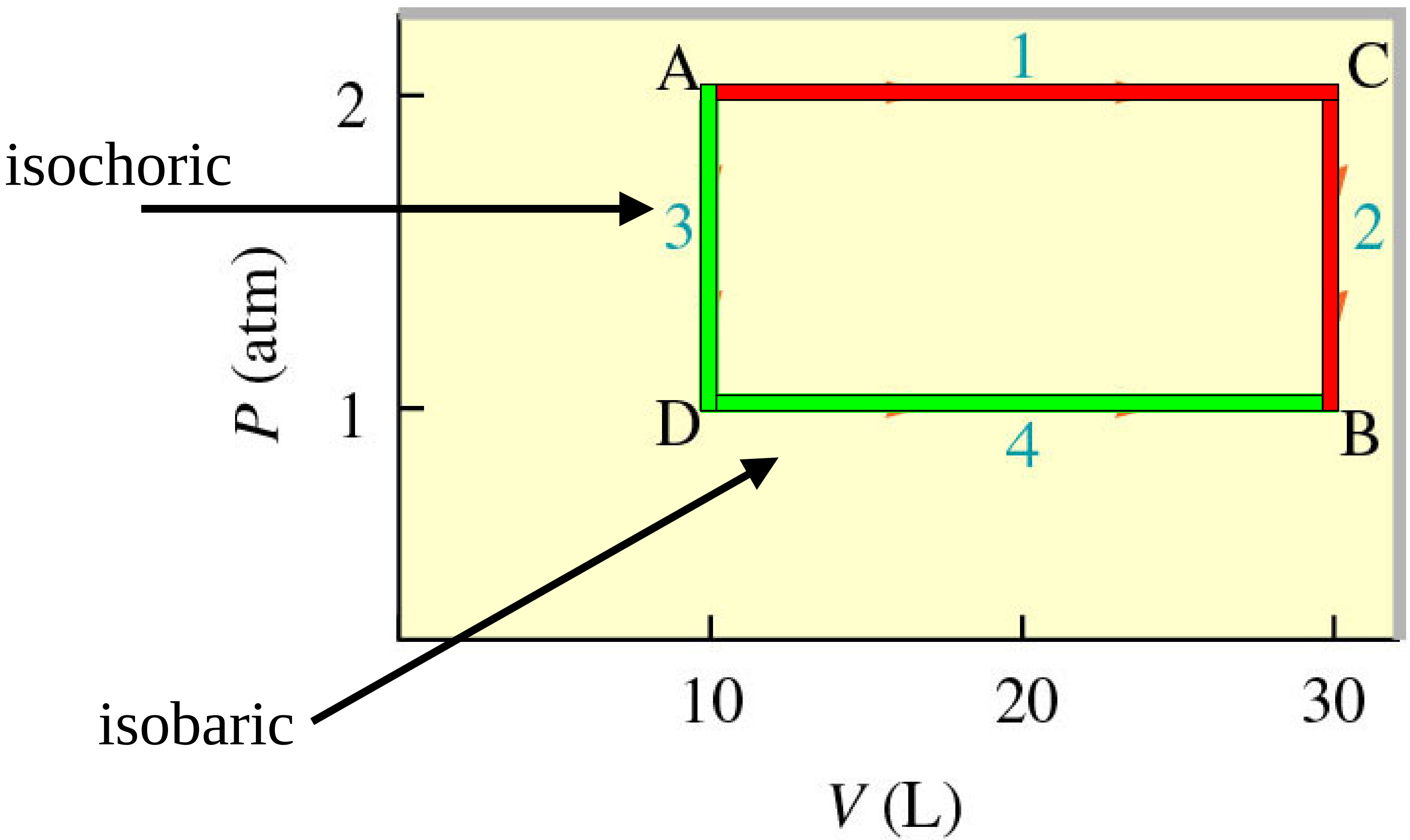
- When doing pathways, we usually keep one variable constant. The language used to indicate what is held constant is:
  - Isobaric: Constant Pressure ($\Delta P=0$)
  - Isothermal: Constant Temperature ($\Delta T=0$)
  - Isochoric: Constant Volume ($\Delta V=0$)
  - Adiabatic: No state variable is held constant but No heat can enter or leave ($q=0$)

Why we need Paths and State Functions

- Our goal is to build an engine , much like a car or refrigerator engine; a thermodynamic engine.
- We need to understand how heat is used to do productive work.
- Need to follow the path the engine takes and the flow of heat and work
- Heat is a product of chemical reactions so we will tie chemical reactions to do productive work
- Need to develop quantities (state functions) that can be tabulated to tell us how much work we can get from a reaction.

Thermodynamic Path:

A series of steps or changes in a system that takes the system from an initial state to a final state



First Pathway -- red A-C-B

Step 1. (A to C) Constant pressure expansion (P = 2 atm) from 10.0 to 30.0 liters. (Different number; Z9.29, Previous Lecture)

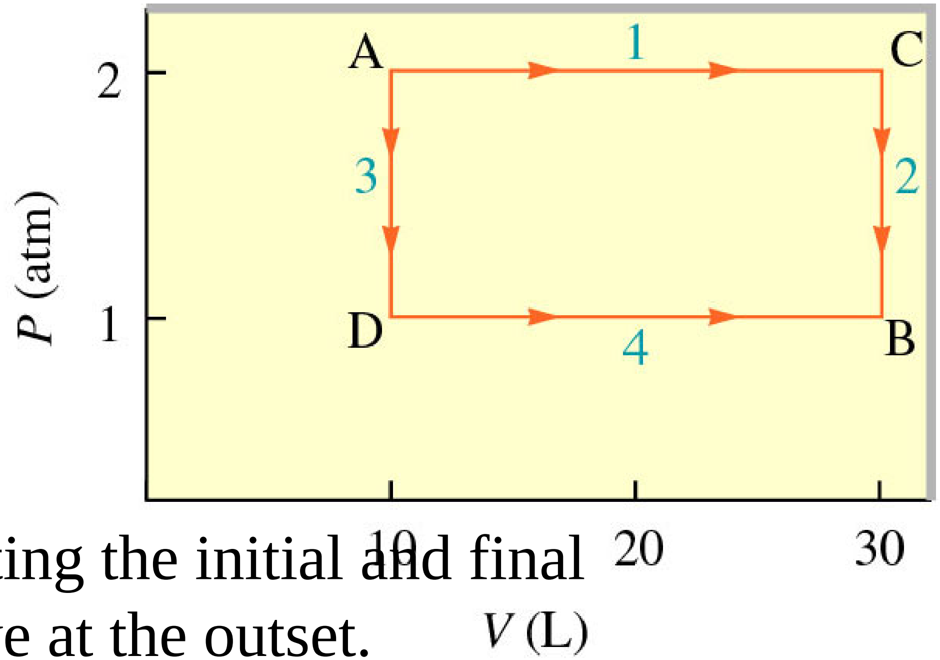
$P\Delta V$ = (2.00 atm)(30.0 l - 10.0 l) = 40.0 l.-atm

= (40.0 l-.atm)(101.3 J/l.atm) = 4.0 x 10^3 J

= -w

And $\Delta T = P\Delta V/nR$ = 4.05 x 10^3 J/(2 mol)(8.314 J/mol.K)

ΔT = 243.6 K



Notice: We did not bother computing the initial and final temperatures, which we could have at the outset.

Pathway 1 Step 1, Other quantities

- Step 1 is isobaric (constant P); therefore,

$\Delta H_1 = nC_p\Delta T = (2\text{mol})(5/2R)(243.6\text{ K})$

$= 1.0 \times 10^4\text{ J} = 10\text{ kJ}$

$\Delta H_1 = q_1 = q_P$

And $\Delta E_1 = nC_v\Delta T = (2\text{mol})(3/2R)(243.6\text{ K})$

$= 6.0 \times 10^3\text{ J} = 6\text{kJ}$

(check: $\Delta E_1 = q_1 + w_1 = (10. \times 10^3\text{ J}) - (4.0 \times 10^3\text{ J})$

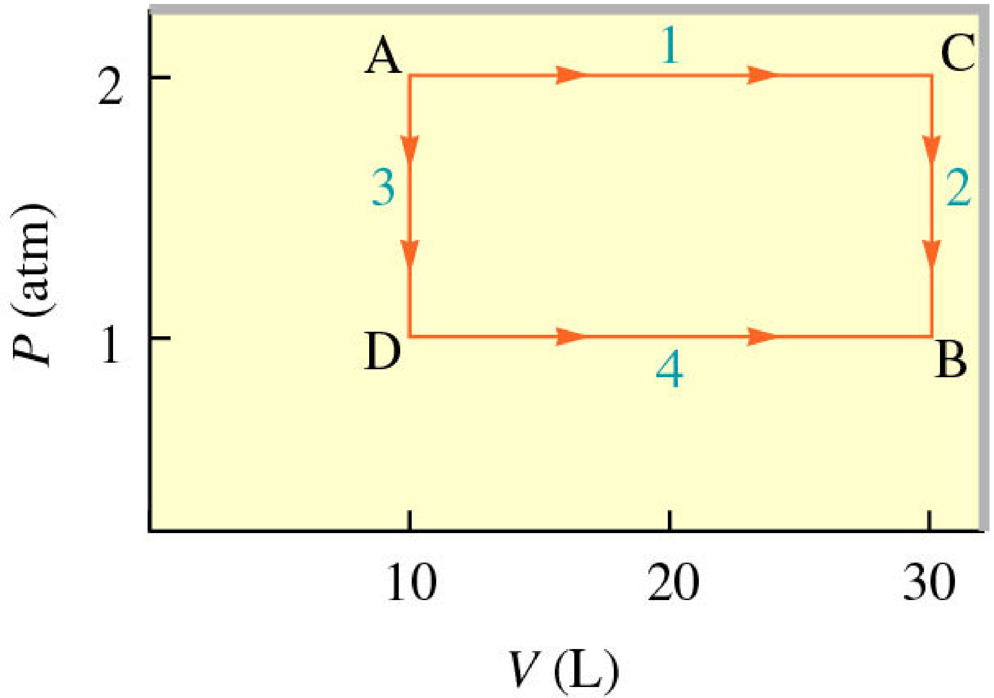
$= 6.0 \times 10^3\text{ J}$)

Pathway 1 Step 2 -- C to B

- Step 2: Isochoric (const. V=30; $\Delta V=0$) cooling until pressure is reduced from 2.00 atm to 1.00 atm. $\Delta P=1-2=-1$Atm
- First, calculate ΔT:
  - Now, $\Delta T = (\Delta P)V/nR$ (note: P changes, not V)

    $= (-1.00 \text{ atm})(30.0 \text{ l})/ (2 \text{ mol})(.0821 \text{ l.atm/mol K})$

    $= -182.7 \text{ K}$
- w=0 (no work)



Pathway 1 Step 2, other quantities

- $\Delta E_2 = nC_v\Delta T = (2\text{ mol})(3/2R)(-182.7\text{ K})$
  $= -4.6 \times 10^3\text{ J}$
- and $\Delta E_2 = nC_v\Delta T = -4.6\text{ kJ} = q_2 = q_v$
- and $\Delta H_2 = nC_p\Delta T = -7.6 \times 10^3\text{ J}$
- Finally $w_2 = 0$ (isochoric…no V change)

Pathway 1 Sum the two steps from A to B (via C)

- Thermodynamic totals for this pathway are the sum of values for step 1 and step 2

ΔT = 243.6-182.7=60.9K

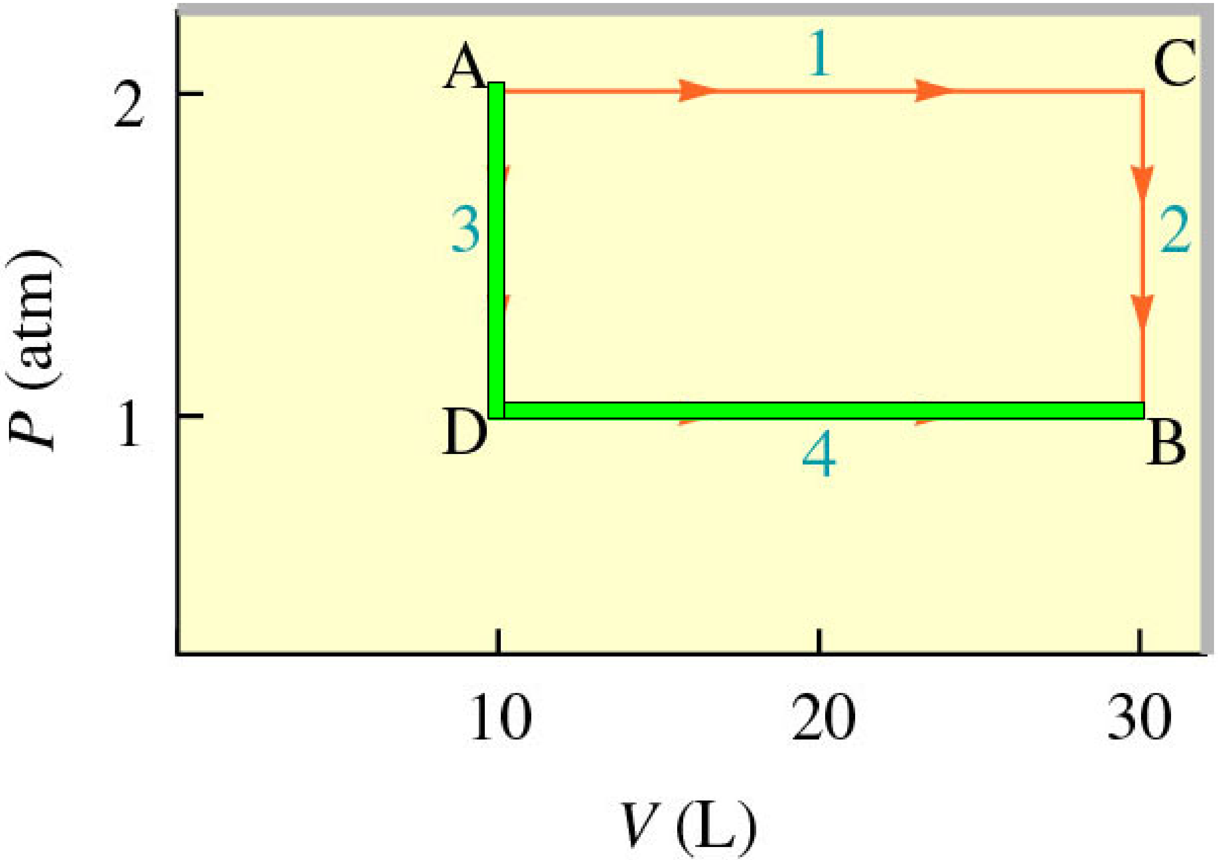
$q = q_1 + q_2 = 5.5$ kJ

$w = w_1 + w_2 = -4.0$ kJ

$\Delta E = \Delta E_1 + \Delta E_2 = 1.5$ kJ

$\Delta H = \Delta H_1 + \Delta H_2 = 2.5$ kJ

Next Pathway – green A to B via D



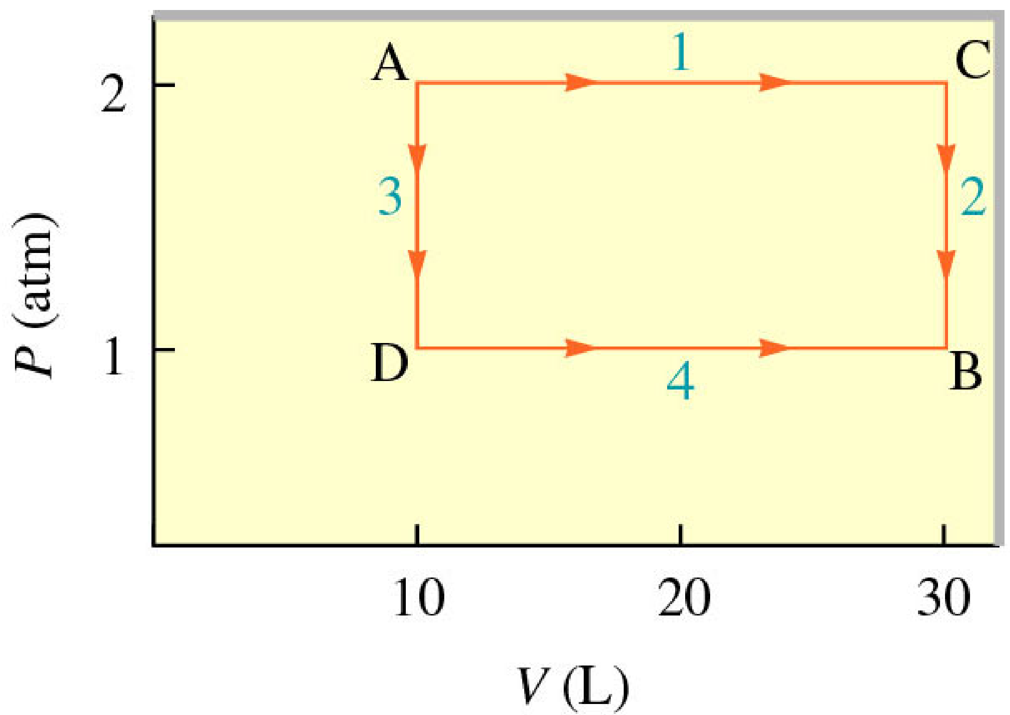
Now we will do the same calculations for the green path.

Pathway 2 Step 1 A to D (Labeled 3)

- Step 1: Isochoric cooling from P = 2.00 atm to P = 1.00 atm. $\Delta P = -1$ atm.
- First, calculate ΔT:

$$\Delta T = \Delta PV/nR = (-1.00 \text{ atm})(10.0 \text{ l})/ (2 \text{ mol})R$$

$$= -60.9 \text{ K}$$



Pathway 2 Step 1

- Then, calculate the rest for Step 1:

$$\Delta E_1 = nC_v\Delta T = (2\ \text{mol})(3/2\ R)(-60.9\ \text{K})$$

$$= -1.5\ \text{k J} = \qquad q_1 = q_v$$

$$\Delta H_1 = nC_P\Delta T = (2\ \text{mol})(5/2\ R)(-60.9\ \text{K})$$

$$= -2.5\ \text{k J}$$

$w_1 = 0$ (constant volume)

Pathway 2 Step 2 (D to B)

- Step 2: Isobaric (constant P) expansion at 1.0 atm from 10.0 l to 30.0 l.
- $\Delta T = P\Delta V/nR = (1 \text{ atm})(20.0 \text{ l})/(2 \text{ mol})R$

  $= 121.8 \text{ K}$

Pathway 2 Step 2

- Then, calculate the rest:

$$\Delta H_2 = nC_P\Delta T = (2\text{ mol})(5/2\text{ R})(121.8\text{ K})$$
$$= 5.1\text{ kJ} = q_2 = q_p$$

$$\Delta E_2 = nC_v\Delta T = (2\text{ mol})(3/2\text{ R})(121.8\text{ K})$$
$$= 3.1\text{ kJ}$$

$$w_1 = -P\Delta V = -20\text{ l-atm} = -2.0\text{ k J}$$

Pathway 2 Sum the two steps from A to B (via D)

- Thermodynamic totals for this pathway are again the sum of values for step 1 and step 2:

$$\Delta T = -60.9 + 121.8 = 60.9 K$$

$$q = q_1 + q_2 = 3.6\ kJ$$

$$w = w_1 + w_2 = -2.0\ kJ$$

$$\Delta E = \Delta E_1 + \Delta E_2 = 1.5\ kJ$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 2.5\ kJ$$

Comparison of Path 1 and Path 2

- Pathway 1

$q = 5.5 \times 10^3$ J

$w = -4.0 \times 10^3$ J

$\Delta E = 1.5 \times 10^3$ J

$\Delta H = 2.5 \times 10^3$ J

- Pathway 2

$q = 3.5 \times 10^3$ J

$w = -2.0 \times 10^3$ J

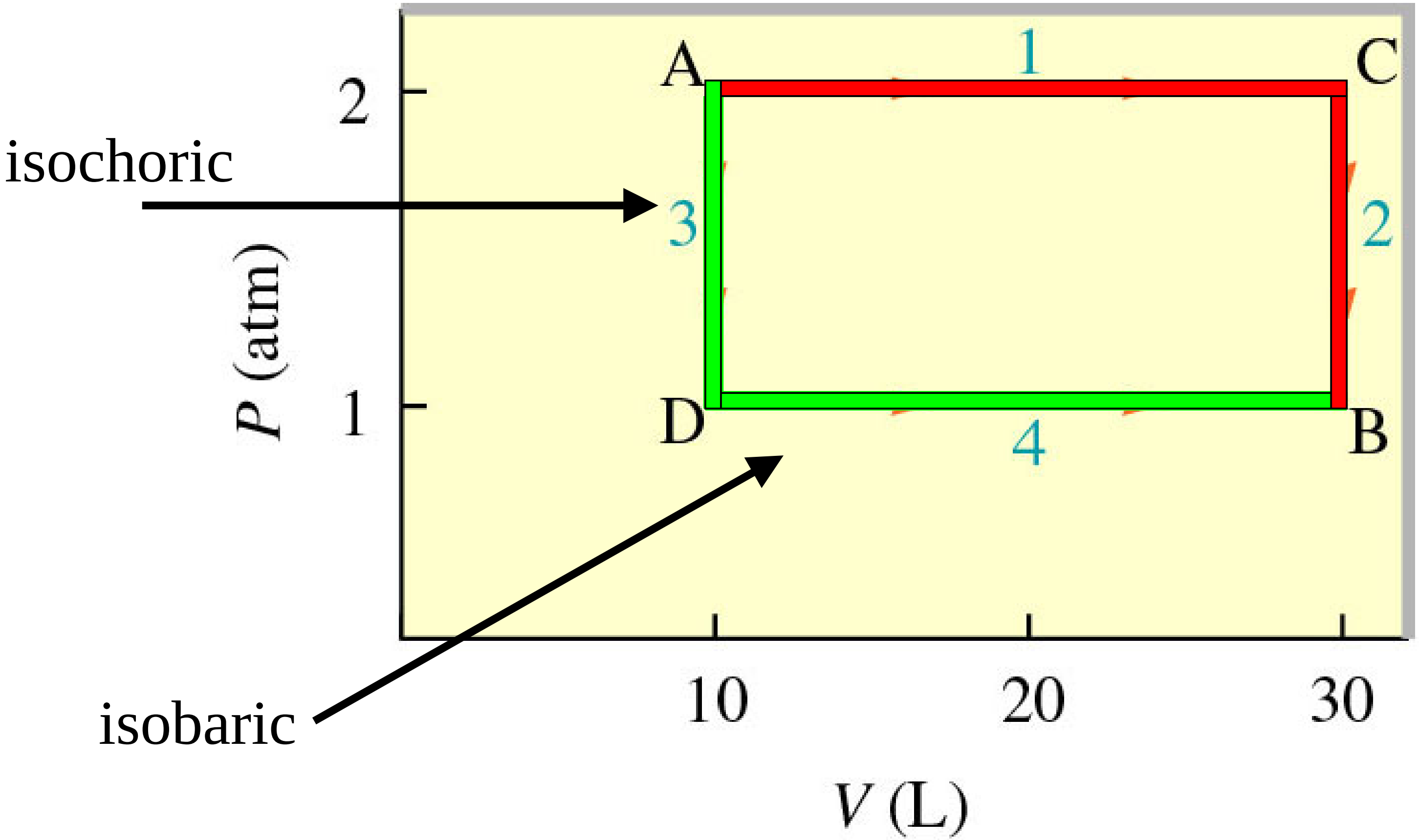
$\Delta E = 1.5 \times 10^3$ J

$\Delta H = 2.5 \times 10^3$ J

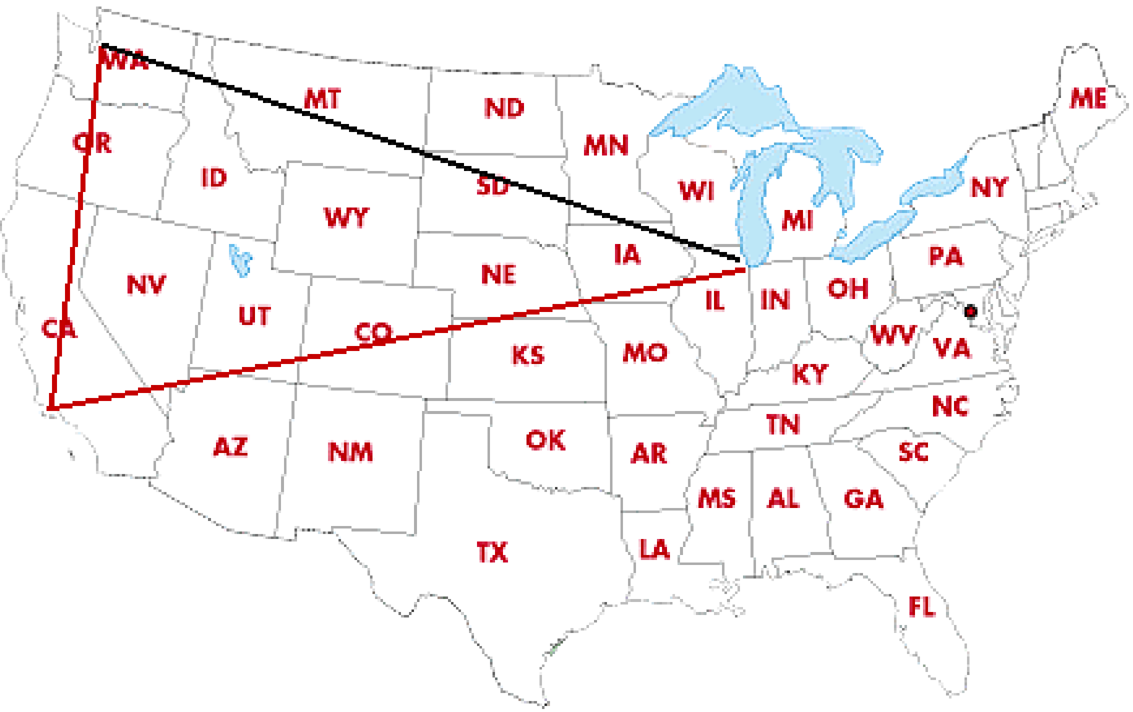
Note: Energy and Enthalpy (like the temperature) are the same;
but heat and work are not the same!

Thermodynamic Path:

A series of steps or changes in a system that takes the system from an initial state to a final state



State Functions



- A **State Function** is a function in which the value only depends on the initial and final state….NOT on the pathway taken.

- In this example, start in Seattle, end in Chicago, but you take different paths to get from one place to the other.

List some quantities that would be dependent on path and some that would be independent of path (state functions).

Thermodynamic State Functions

- Thermodynamic State Functions: Thermodynamic properties that are dependent on the state of the system only. (Example: ΔE and ΔH)

- Other variables will be dependent on pathway (Example: q and w). These are NOT state functions. The pathway from one state to the other must be defined.