

Thermodynamics of an Ideal Gas

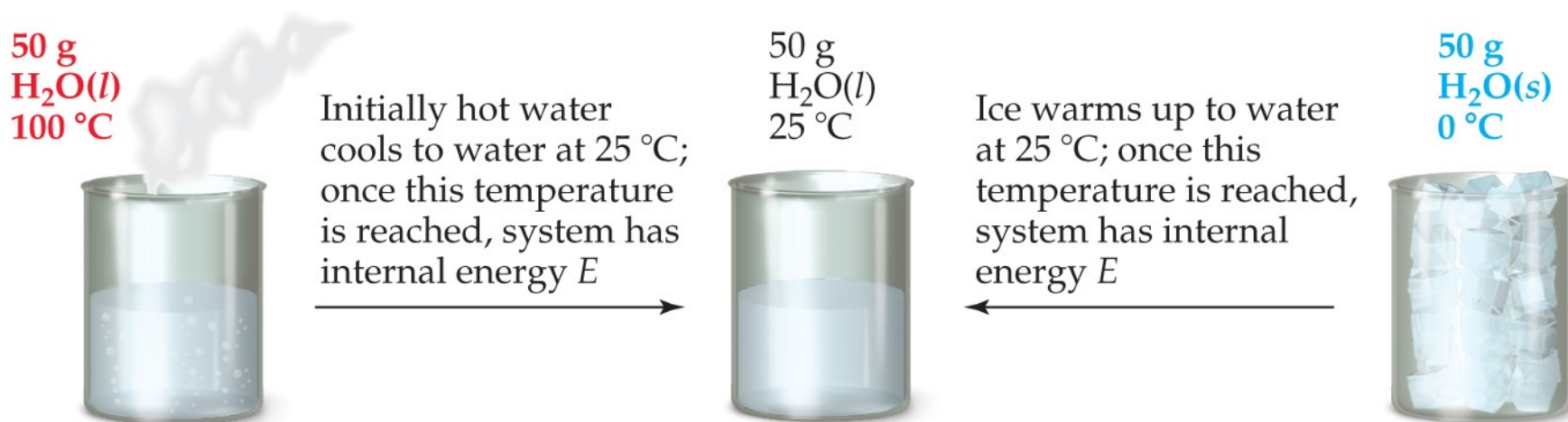
A State Function

Does not depend on how the system arrived at its present state; only on the characteristics of the present state.

Volume, Pressure, Temperature, ΔE , ΔH

State Functions

Usually we have no way of knowing the internal energy of a system; finding that value is simply too complex a problem.



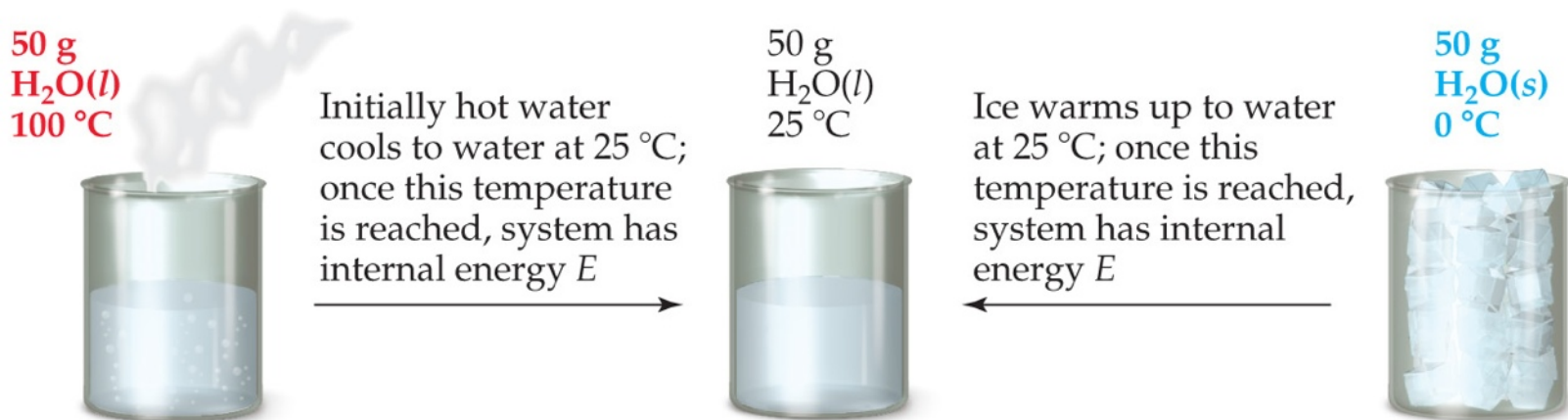
© 2012 Pearson Education, Inc.



© 2012 Pearson Education, Inc.

State Functions

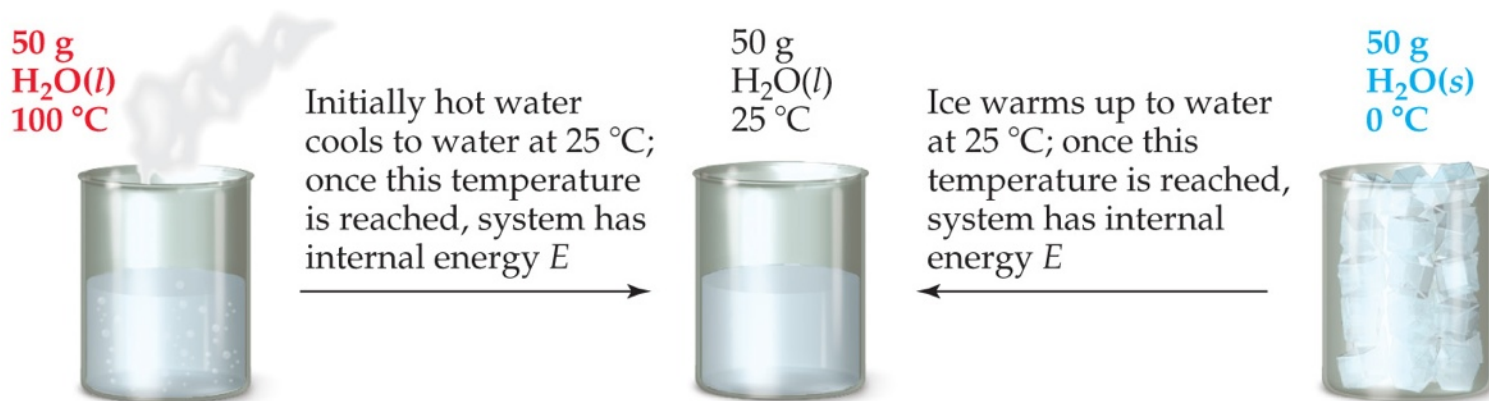
- However, we do know that the internal energy of a system is independent of the path by which the system achieved that state.
 - In the system depicted in Figure 5.9, the water could have reached room temperature from either direction.



© 2012 Pearson Education, Inc.

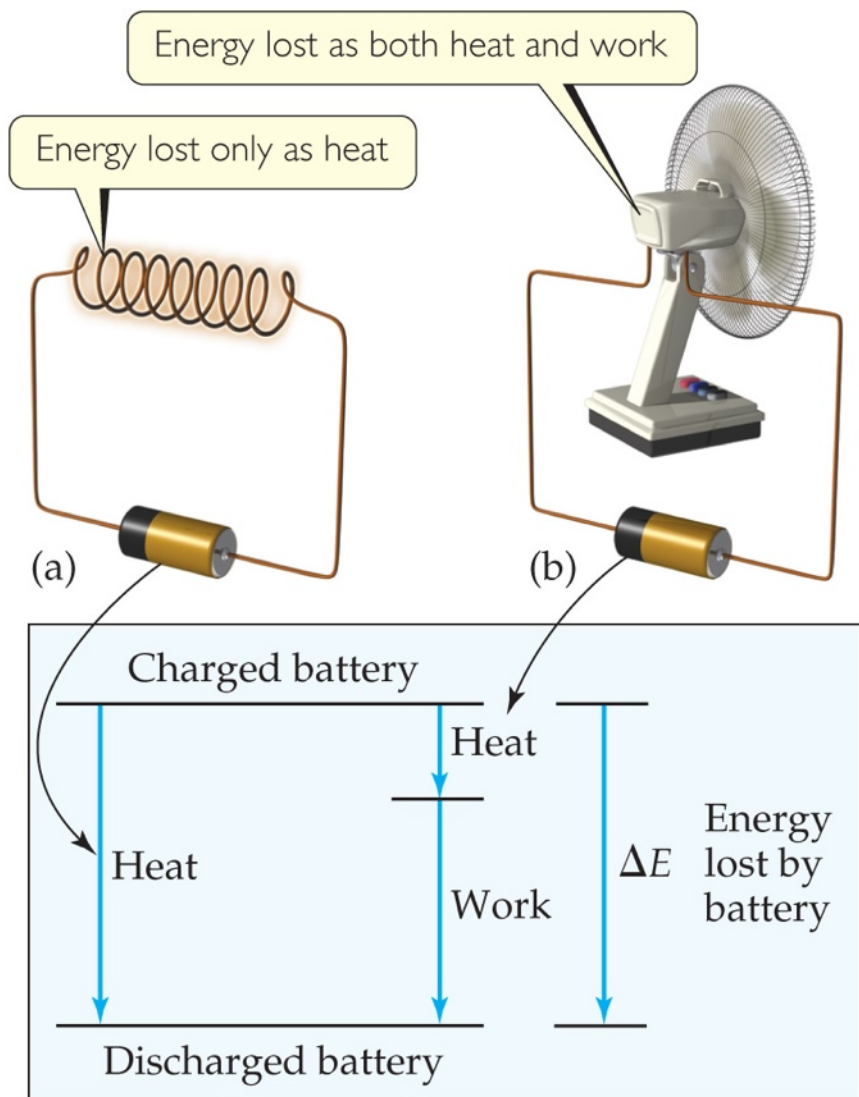
State Functions

- Therefore, internal energy is a state function.
- It depends only on the present state of the system, not on the path by which the system arrived at that state.
- And so, ΔE depends only on E_{initial} and E_{final} .



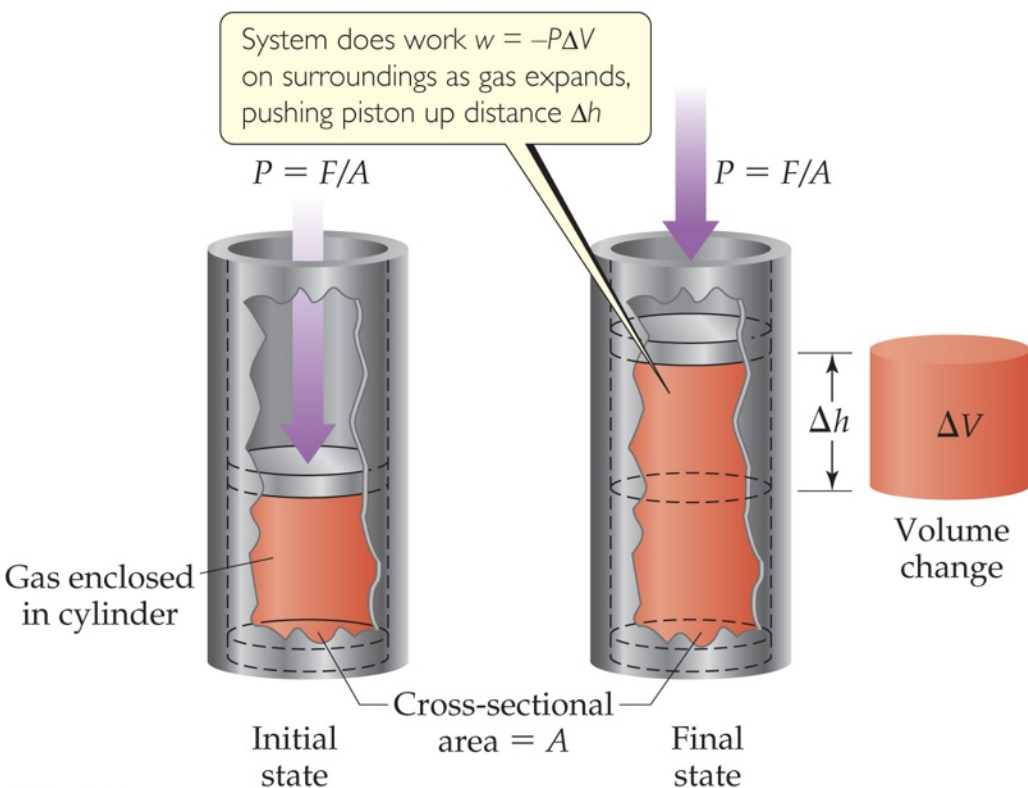
© 2012 Pearson Education, Inc.

State Functions



- However, q and w are *not* state functions.
- Whether the battery is shorted out or is discharged by running the fan, its ΔE is the same.
 - But q and w are different in the two cases.

Work

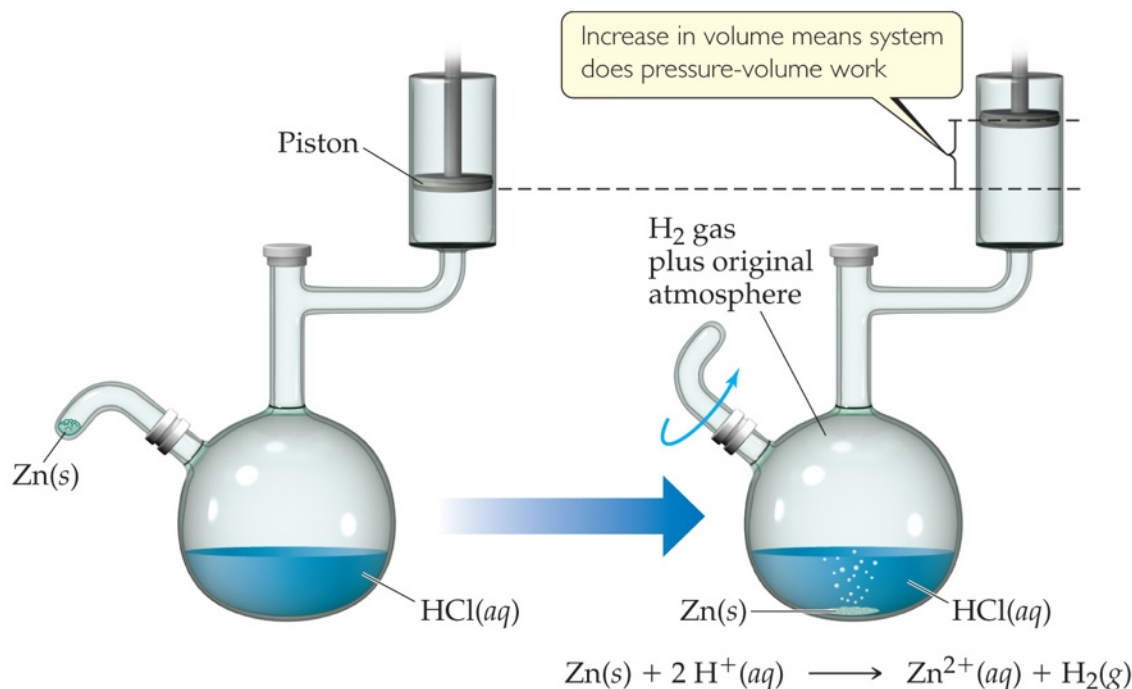


Usually in an open container the only work done is by a gas pushing on the surroundings (or by the surroundings pushing on the gas).

Work

We can measure the work done by the gas if the reaction is done in a vessel that has been fitted with a piston:

$$w = -P\Delta V$$



© 2012 Pearson Education, Inc.

© 2012 Pearson Education, Inc.



Thermochemistry

Ideal Gas

The hypothetical condition approached by real gases at high temperatures and low pressures $(PV = nRT)$

The average translational energy for one mole of gas at a given temperature in Kelvins

$$(\text{KE})_{\text{ave}} = \frac{3}{2} RT$$

Ideal Gas

The hypothetical condition approached by real gases at high temperatures and low pressures $(PV = nRT)$

The average **translational** energy for one mole of gas at a given temperature in Kelvins

$$(\mathbf{KE})_{\text{ave}} = \frac{3}{2} RT$$

Molar Heat Capacity (C)

The energy required to raise the temperature of 1mole of a substance by 1K.

$$q = n C \Delta T$$

heat ————— q = n C ΔT ————— change in temperature

moles

Molar Heat Capacity (C)

The energy required to raise the temperature of 1mole of a substance by 1K.

heat

$$q = n C \Delta T$$

change in
temperature

J/mol K

moles

Heating an Ideal Gas at constant volume

$$(\text{KE})_{\text{ave}} = \frac{3}{2} RT$$

$$(\text{heat energy required}) = \frac{3}{2} RT$$

No change in volume - no work done

$$C_v = \frac{3}{2} R$$

heat energy required to change the temp. of one mole of monoatomic gas 1 K at constant volume

Heating an Ideal Gas at constant pressure

the volume increases work is done

**(heat energy
required) =**

**(heat energy required to
change the translation
energy)**

+

**(the energy needed
to do the PV work)**

Heating an Ideal Gas at constant pressure

the volume increases work is done

$$\text{(heat energy required)} = \frac{3}{2} R + P\Delta V$$

$$P\Delta V = nR\Delta T \\ = R$$

For a 1 mole 1 K change

$$C_p = \frac{3}{2} R + R$$

$$C_p = C_v + R$$

heat energy required to change the temp. of one mole of monoatomic gas 1 K at constant pressure

Heating a Polyatomic Gas

polyatomic gases absorb energy to excite rotational and vibrational motions in addition to translational motions causing higher C_v than $(3/2)R$

$$C_p = C_v + R$$

Assuming ideal behavior if C_v is known C_p can be calculated for any gas

Heating a Gas and Energy

$$\Delta E = \frac{3}{2} R \Delta T \quad \text{for } n \text{ moles}$$

$$\Delta E = C_v \Delta T \quad \Delta E = n C_v \Delta T$$

At constant pressure work is done

(heat energy required) = $q_p = n C_p \Delta T$

$$= n(C_v + R) \Delta T$$

$$\Delta H = \underbrace{n C_v \Delta T}_{\Delta E} + \underbrace{n R \Delta T}_{P \Delta V}$$

Heating a Gas and Enthalpy

$$H = E + PV$$

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

$$\Delta H = \Delta E + nR\Delta T$$

$$\Delta H = nC_v\Delta T + nR\Delta T$$

$$\Delta H = n(C_v + R) \Delta T$$

$$\Delta H = nC_p\Delta T$$

Summary

$$q = nC \Delta T$$

$$\Delta E = nC_v \Delta T$$

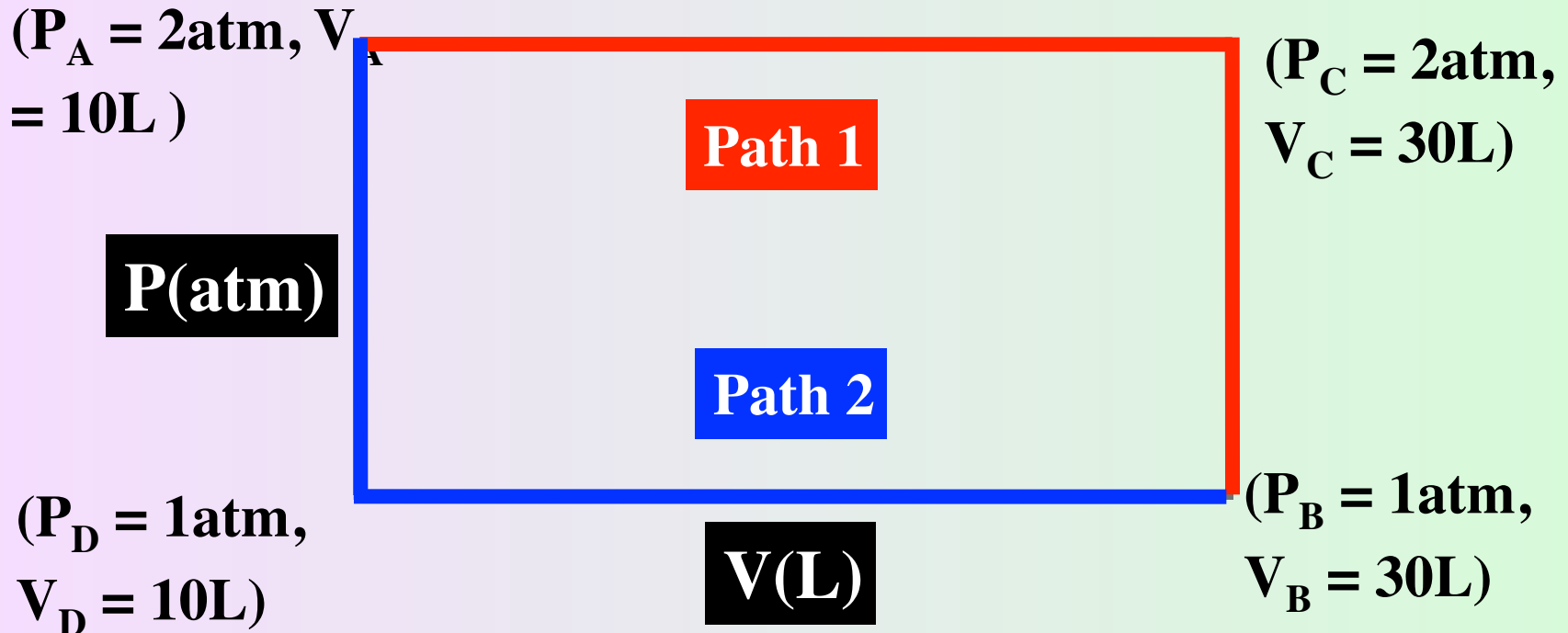
$$\Delta H = nC_p \Delta T$$

$$C_v = \frac{3}{2} R$$

$$C_p = C_v + R$$

Example: Heating an Ideal Gas

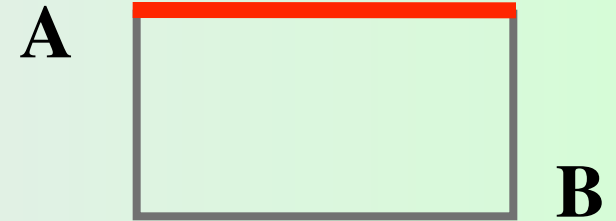
Consider 2.00 mol of a monoatomic ideal gas that is taken from state A ($P_A = 2\text{atm}$, $V_A = 10\text{L}$) to state B ($P_B = 1\text{atm}$, $V_B = 30\text{L}$) by two different pathways: calculate q , w , ΔE , and ΔH for the two pathways



Step 1

$$V_A = 10L \quad V_C = 30L$$

At constant pressure = 2atm



$$P\Delta V = nR\Delta T$$

$$P\Delta V = (2\text{atm})(20L) = 40 \text{ atm L} \times \frac{101.3 \text{ J}}{1\text{atmL}} = 4.05 \times 10^3 \text{ J}$$

$$nR\Delta T = 4.05 \times 10^3 \text{ J}$$

$$\Delta T = \frac{4.05 \times 10^3 \text{ J}}{nR}$$

$$w = -P\Delta V = -4.05 \times 10^3 \text{ J}$$

$$\Delta H = q_p = 1.01 \times 10^4 \text{ J}$$

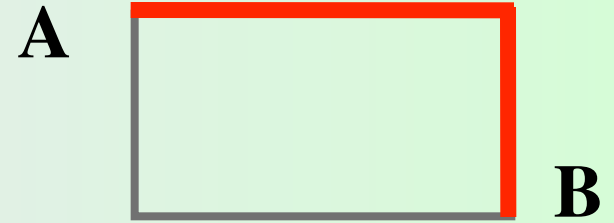
$$q_p = nC_p\Delta T = n \left(\frac{5}{2} R \right) \left(\frac{4.05 \times 10^3 \text{ J}}{nR} \right) = 1.01 \times 10^4 \text{ J}$$

$$\Delta E = nC_v\Delta T = n \left(\frac{3}{2} R \right) \left(\frac{4.05 \times 10^3 \text{ J}}{nR} \right) = 6.08 \times 10^3 \text{ J}$$

Step 2

$$P_C = 2\text{atm} \quad P_B = 1\text{atm}$$

At constant volume = 30L



$$\Delta PV = nR\Delta T \quad \Delta T = \frac{\Delta PV}{nR}$$

$$\Delta T = \frac{(30\text{L})(1\text{atm} - 2\text{atm})}{nR} = \frac{-30 \text{ atmL}}{nR} \times \frac{101.3 \text{ J}}{1\text{atmL}} = \frac{-3.04 \times 10^3 \text{ J}}{nR}$$

$w = 0$ (no change in volume)

$$q_v = nC_v\Delta T = n \left(\frac{3}{2} R \right) \left(\frac{-3.04 \times 10^3 \text{ J}}{nR} \right) = -4.56 \times 10^3 \text{ J}$$

$$\Delta E = q_v$$

$$\Delta H = nC_p\Delta T = n \left(\frac{5}{2} R \right) \left(\frac{-3.04 \times 10^3 \text{ J}}{nR} \right) = -7.6 \times 10^3 \text{ J}$$

Step 3

$$P_C = 2\text{atm} \quad P_B = 1\text{atm}$$

At constant volume = 10L



$$\Delta PV = nR\Delta T \quad \Delta T = \frac{\Delta PV}{nR}$$

$$\Delta T = \frac{(10\text{L})(1\text{atm} - 2\text{atm})}{nR} = \frac{-10 \text{ atmL}}{nR} \times \frac{101.3 \text{ J}}{1\text{atmL}} = \frac{-1.01 \times 10^3 \text{ J}}{nR}$$

$w = 0$ (no change in volume)

$$q_v = nC_v\Delta T = n \left(\frac{3}{2} R \right) \left(\frac{-1.01 \times 10^3 \text{ J}}{nR} \right) = -1.52 \times 10^3 \text{ J}$$

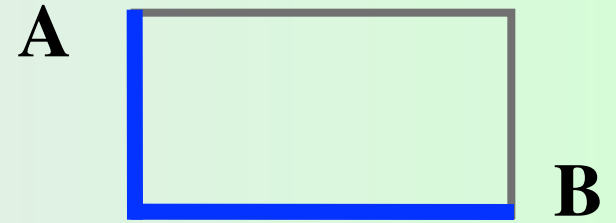
$$\Delta E = q_v$$

$$\Delta H = nC_p\Delta T = n \left(\frac{5}{2} R \right) \left(\frac{-1.01 \times 10^3 \text{ J}}{nR} \right) = -5.08 \times 10^3 \text{ J}$$

Step 4

$$V_A = 10L \quad V_C = 30L$$

At constant pressure = 1atm



$$P\Delta V = nR\Delta T$$

$$P\Delta V = (1\text{atm})(20L) = 20 \text{ atm L} \times \frac{101.3 \text{ J}}{1\text{atmL}} = 2.03 \times 10^3 \text{ J}$$

$$nR\Delta T = 2.03 \times 10^3 \text{ J}$$

$$\Delta T = \frac{2.03 \times 10^3 \text{ J}}{nR}$$

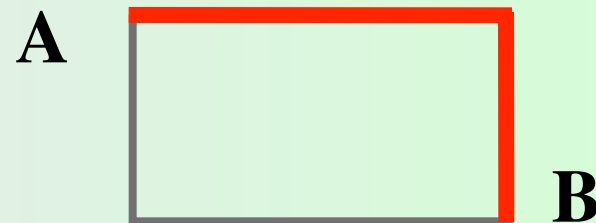
$$w = -P\Delta V = -2.03 \times 10^3 \text{ J}$$

$$\Delta H = q_p = 5.08 \times 10^3 \text{ J}$$

$$q_p = nC_p\Delta T = n \left(\frac{5}{2} R \right) \left(\frac{2.03 \times 10^3 \text{ J}}{nR} \right) = 5.08 \times 10^3 \text{ J}$$

$$\Delta E = nC_v\Delta T = n \left(\frac{3}{2} R \right) \left(\frac{2.03 \times 10^3 \text{ J}}{nR} \right) = 6.08 \times 10^3 \text{ J}$$

Pathway One



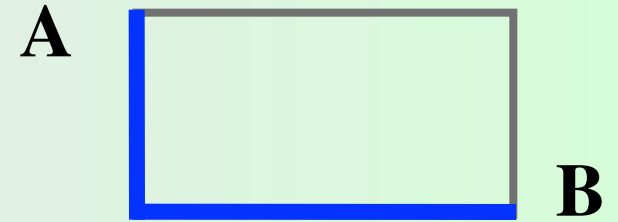
$$w = w_1 + w_2 = -4.05 \times 10^3 \text{ J} + 0$$

$$q = q_1 + q_2 = -4.56 \times 10^3 \text{ J} + 1.01 \times 10^4 \text{ J} = 5.5 \times 10^3 \text{ J}$$

$$\Delta E = q + w = 5.50 \times 10^3 \text{ J} - 4.05 \times 10^3 \text{ J} = 1.50 \times 10^3 \text{ J}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 1.01 \times 10^4 \text{ J} + 7.6 \times 10^3 \text{ J} = 2.50 \times 10^4 \text{ J}$$

Pathway Two



$$w = w_3 + w_4 = 0 - 2.03 \times 10^3 \text{ J}$$

$$q = q_3 + q_4 = -1.52 \times 10^3 \text{ J} + 5.08 \times 10^4 \text{ J} = 3.56 \times 10^3 \text{ J}$$

$$\Delta E = q + w = 3.56 \times 10^3 \text{ J} - 2.03 \times 10^3 \text{ J} = 1.5 \times 10^3 \text{ J}$$

$$\Delta H = \Delta H_3 + \Delta H_4 = 2.53 \times 10^3 \text{ J} + 5.08 \times 10^3 \text{ J} = 2.55 \times 10^3 \text{ J}$$

$$w = -4.05 \times 10^3 \text{ J}$$

$$q = 5.5 \times 10^3 \text{ J}$$

$$\Delta E = 1.50 \times 10^3 \text{ J}$$

$$\Delta H = 2.50 \times 10^3 \text{ J}$$

($P_A = 2 \text{ atm}$, $V_A = 10 \text{ L}$)

P(atm)

Path 1

Path 2

($P_B = 1 \text{ atm}$,

$V_B = 30 \text{ L}$)

$$w = -2.03 \times 10^3 \text{ J}$$

$$q = 3.56 \times 10^3 \text{ J}$$

$$\Delta E = 1.5 \times 10^3 \text{ J}$$

$$\Delta H = 2.55 \times 10^3 \text{ J}$$

V(L)