

Chemistry 163B

Lecture 5

Winter 2013

Challenged Penmanship

Notes

## First Law: ideal gas calculations

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relationships that apply to **ideal gasses** for all conditions with  $w_{\text{other}}=0$  and constant composition (some also apply more generally):

$\Delta U = q + w$	$w = -\int P_{\text{ext}} dV$	$PV = nRT$
$q_V = n \int \bar{C}_V dT$ $\quad ?$ $\quad = n \bar{C}_V \Delta T$	$q_P = n \int \bar{C}_P dT$ $\quad ?$ $\quad = n \bar{C}_P \Delta T$	$\bar{C}_P = \bar{C}_V + R$
$H \equiv U + PV$		
<b>monatomic ideal gas</b>	$\bar{C}_V = \frac{3}{2}R$	$\bar{C}_P = \frac{5}{2}R$

*first law calculations for **ideal gas** no work other, constant n:*

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show:  $\Delta U_{\text{any conditions}} = n\bar{C}_V\Delta T$        $\Delta H_{\text{any conditions}} = n\bar{C}_P\Delta T$

$$dU = n\bar{C}_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

general

but  $\left(\frac{\partial U}{\partial V}\right)_T = 0$       ideal gas

so  $dU = n\bar{C}_V dT$  } ideal gas even  
 $\Delta U = n\bar{C}_V \Delta T$  } if V or P not constant

$$H \equiv U + PV = U + nRT$$

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

$$\Delta H = n\bar{C}_V\Delta T + nR\Delta T$$

$$\Delta H = n(\bar{C}_V + R)\Delta T = n\bar{C}_P\Delta T$$

ideal gas even  
if P or V not constant

isothermal reversible expansion  $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$  at 300K

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$$V = \frac{nRT}{P}$$

$$\Delta U = n\bar{C}_V\Delta T \quad \Delta H = n\bar{C}_P\Delta T$$

$$\Delta U = 0 \quad \Delta H = 0$$

$$\Delta U = 0 \Rightarrow q = -w$$

$$w = -\int_{V_1}^{V_2} PdV = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$$

$$w = (1 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln\left(\frac{1 \text{ atm}}{10 \text{ atm}}\right)$$

$$w = -5.743 \text{ kJ} \quad \text{and} \quad q = 5.743 \text{ kJ}$$

did  
earlier

**NOTE:**  $\Delta H \neq q$

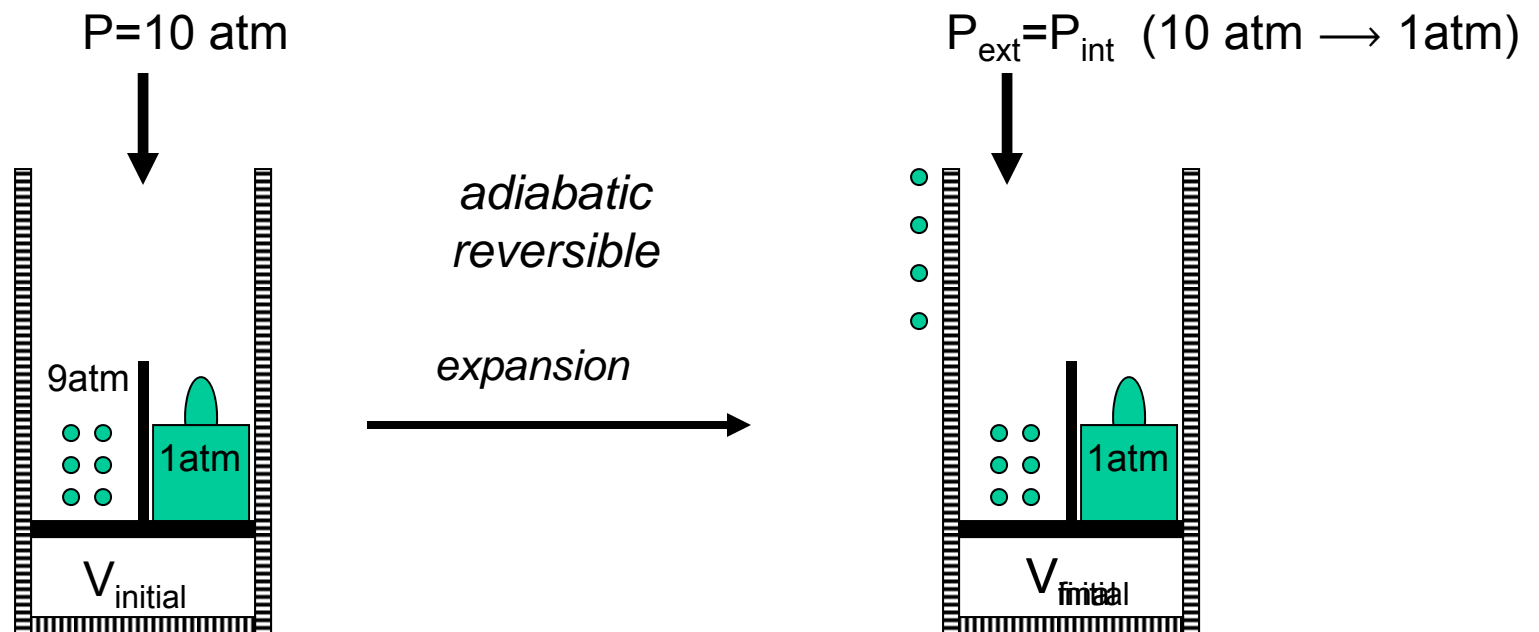
why ???  
\* \* \*

## First Law: ideal gas calculations

relationships that apply to **ideal gasses** for all conditions with  $w_{\text{other}}=0$  and constant composition (some also apply more generally):

$\Delta U = q + w$	$w_{PV} = -\int P_{ext} dV$	$PV = nRT$
$q_V = n \int \bar{C}_V dT$ ? $= n \bar{C}_V \Delta T$	$q_P = n \int \bar{C}_P dT$ ? $= n \bar{C}_P \Delta T$	$\bar{C}_P = \bar{C}_V + R$
$H \equiv U + PV$	$\Delta U_{\text{any conditions}} = n \bar{C}_V \Delta T$	$\Delta H_{\text{any conditions}} = n \bar{C}_P \Delta T$
<b>monatomic ideal gas</b>	$\bar{C}_V = \frac{3}{2}R$	$\bar{C}_P = \frac{5}{2}R$

## Pressure-Volume work reversible adiabatic expansion



- $q=0$
- $w = - \int P_{\text{ext}} dV$
- $\Delta U = q + w$
- $\Delta V > 0 \Rightarrow w < 0$  ( $w_{\text{surr}} > 0$ )
- $\Delta U = w < 0 \Rightarrow$  gas cools as  $V$  increases

## *adiabatic processes and the First Law*

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$$q = 0$$

$$\Delta U = w$$

expansion  $\Delta V > 0$   $-\int PdV = w < 0$   $\Delta U < 0$  (ideal gas) system cools

compression  $\Delta V < 0$   $-\int PdV = w > 0$   $\Delta U > 0$  (ideal gas) system warms

## ideal gas adiabatic reversible processes WORK

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$$w = - \int_{\text{initial}}^{\text{final}} P_{\text{ext}} dV$$

**work**

$$P_{\text{ext}} = P_{\text{int}} = P$$

**reversible**

$$P = \frac{nRT}{V}$$

**ideal gas**

so as before ??:

$$w = - \int_{\text{initial}}^{\text{final}} \frac{nRT}{V} dV \neq nRT \int_{\text{initial}}^{\text{final}} \frac{dV}{V}$$

$$w = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$$



but T varies along  
path initial → final



*equate  $dU$  and work for reversible adiabatic process  $P_{\text{ext}}=P_{\text{int}}=P$*

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$$dU = \delta w = -PdV$$

$$dU = n\bar{C}_V dT = -PdV \quad (\text{ideal gas})$$

$$n\bar{C}_V dT = -\frac{nRT}{V} dV$$

$$\frac{\bar{C}_V}{R} \frac{dT}{T} = -\frac{dV}{V}$$

$$\int_{T_1=T_{\text{initial}}}^{T_2=T_{\text{final}}} \frac{\bar{C}_V}{R} \frac{dT}{T} = -\int_{V_1=V_{\text{initial}}}^{V_2=V_{\text{final}}} \frac{dV}{V}$$

$$\frac{\bar{C}_V}{R} \ln \frac{T_{\text{final}}}{T_{\text{initial}}} = -\ln \frac{V_{\text{final}}}{V_{\text{initial}}} = \ln \frac{V_{\text{initial}}}{V_{\text{final}}}$$

*or*

$$\frac{\bar{C}_V}{R} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1} = \ln \frac{V_1}{V_2}$$

*for adiabatic, reversible, ideal gas:  $TvsV$*

$$\left(\frac{T_2}{T_1}\right)^{\bar{c}_v/R} = \left(\frac{V_1}{V_2}\right)$$

$$\frac{\bar{C}_V}{R} \ln \frac{T_2}{T_1} = \ln \frac{V_1}{V_2}$$

$$\ln \left(\frac{T_2}{T_1}\right)^{\frac{\bar{C}_V}{R}} = \ln \frac{V_1}{V_2}$$

$$\left(\frac{T_2}{T_1}\right)^{\frac{\bar{C}_V}{R}} = \frac{V_1}{V_2}$$

$$T_2^{\frac{\bar{C}_V}{R}} V_2 = T_1^{\frac{\bar{C}_V}{R}} V_1$$

**for any two states  $(T_1, V_1, P_1)$  and  $(T_2, V_2, P_2)$   
along an adiabatic reversible path**

**(other)  $T$ vs $P$  relationship for adiabatic reversible (HW#15)**

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$$T_2^{\frac{\bar{C}_V}{R}} V_2 = T_1^{\frac{\bar{C}_V}{R}} V_1$$

with

$$\bar{C}_P = \bar{C}_V + R \quad \text{and} \quad V = \frac{nRT}{P}$$

$$T_2^{\frac{\bar{C}_V}{R}} V_2 = T_1^{\frac{\bar{C}_V}{R}} V_1$$

$$T_2^{\frac{\bar{C}_V}{R}} \frac{nRT_2}{P_2} = T_1^{\frac{\bar{C}_V}{R}} \frac{nRT_1}{P_1}$$

$$T_2^{\frac{\bar{C}_V}{R}+1} P_1 = T_1^{\frac{\bar{C}_V}{R}+1} P_2$$

$$T_2^{\frac{\bar{C}_V+R}{R}} P_1 = T_1^{\frac{\bar{C}_V+R}{R}} P_2$$

$$T_2^{\frac{\bar{C}_P}{R}} P_1 = T_1^{\frac{\bar{C}_P}{R}} P_2$$

$$\frac{T_2^{\frac{\bar{C}_P}{R}}}{P_2} = \frac{T_1^{\frac{\bar{C}_P}{R}}}{P_1}$$

for any two states  $(T_1, V_1, P_1)$  and  $(T_2, V_2, P_2)$   
along an adiabatic reversible path

*summarizing (and HW #15)*

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$$T_2^{\bar{C}_V} V_2 = T_1^{\bar{C}_V} V_1$$

*and*

$$\frac{T_2^{\bar{C}_P}}{P_2} = \frac{T_1^{\bar{C}_P}}{P_1}$$

*and*

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \text{where } \gamma = \frac{\bar{C}_P}{\bar{C}_V}$$

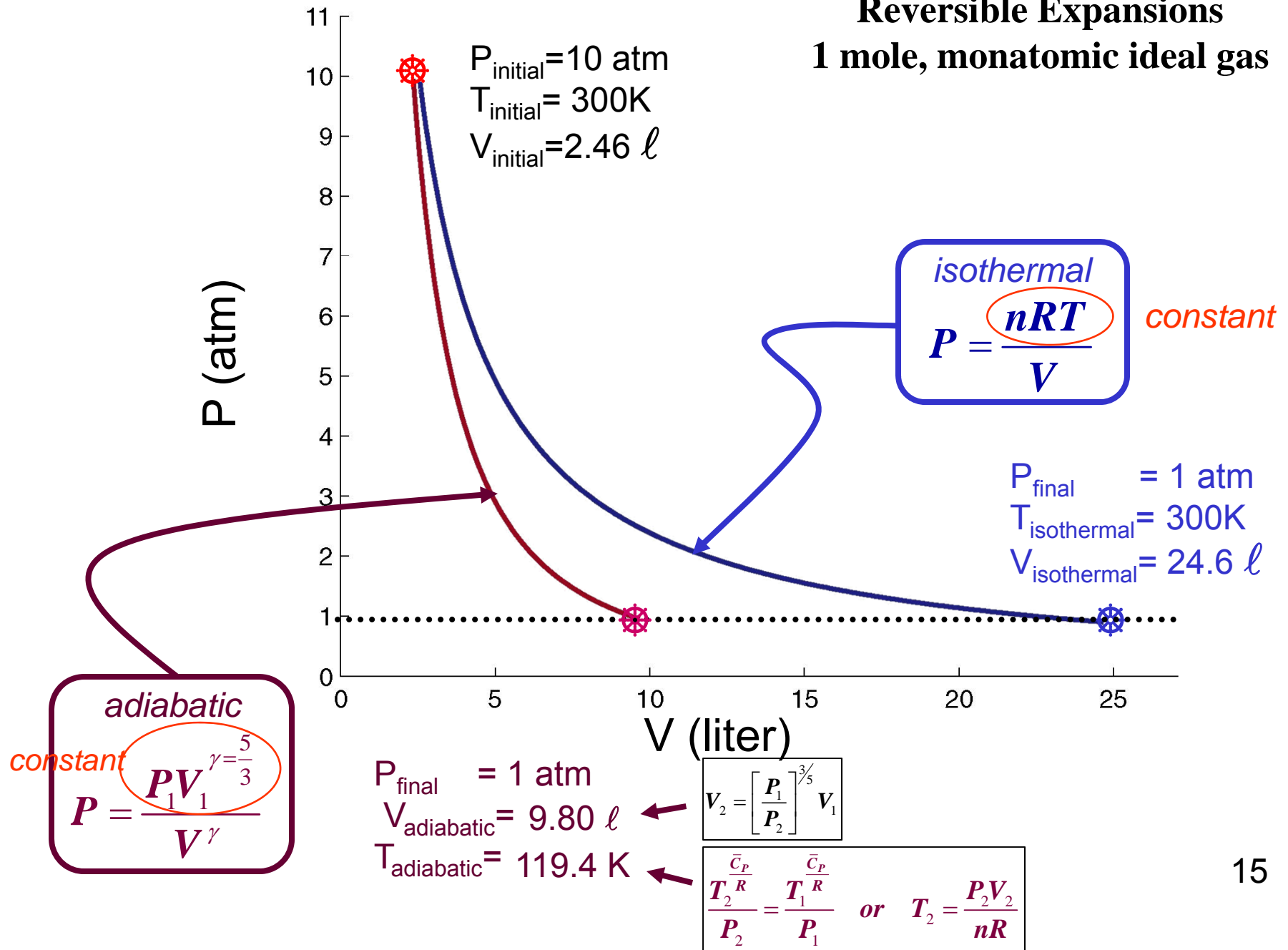
***TvsV***

***TvsP***

***PvsV***

for any two states  $(T_1, V_1, P_1)$  and  $(T_2, V_2, P_2)$   
along an adiabatic reversible path

## Reversible Expansions 1 mole, monatomic ideal gas



adiabatic reversible expansion:  $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$

$P_1 = 10 \text{ atm}$   
 $T_1 = 300 \text{ K}$

$P_2 = 1 \text{ atm}$   
 $T_2 = ???$

use **TvsP**

$$\frac{T_2^{\frac{\bar{C}_P}{R}}}{P_2} = \frac{T_1^{\frac{\bar{C}_P}{R}}}{P_1} \quad \frac{\bar{C}_P}{R} = \frac{5}{2}$$

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{R}{\bar{C}_P}}$$

$$T_2 = T_1 \left( \frac{1 \text{ atm}}{10 \text{ atm}} \right)^{\frac{2}{5}} = 300 \text{ K} \times (0.1)^{\frac{2}{5}}$$

$$T_2 = 300 \text{ K} \times (0.398) = 119.4 \text{ K}$$

calc

$\Delta U, \Delta H$

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = (119.4 - 300) \text{ K} = -180.6 \text{ K}$$

$$\Delta U = n\bar{C}_V\Delta T = (1 \text{ mol}) (1.5) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(-180.6 \text{ K})$$

$$\Delta U = -2.257 \text{ kJ}$$

$$\Delta H = n\bar{C}_P\Delta T = -3.762 \text{ kJ}$$

$$q = 0$$

calc

$q, w$

$$q + w = \Delta U \Rightarrow w = -2.257 \text{ kJ}$$

vs  $-5.743 \text{ kJ}$  for isothermal reversible  
 $10 \text{ atm} \rightarrow 1 \text{ atm}$  at  $300 \text{ K}$

## HW#2 Problem 10 (Raff 2.14)

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10. [from Raff #2.14] One mole of an ideal gas at a temperature of 500 K and a pressure of 6 atm is subjected to the following changes:

**STEP 1:** The gas is expanded isothermally and reversibly to a final pressure of 5atm.

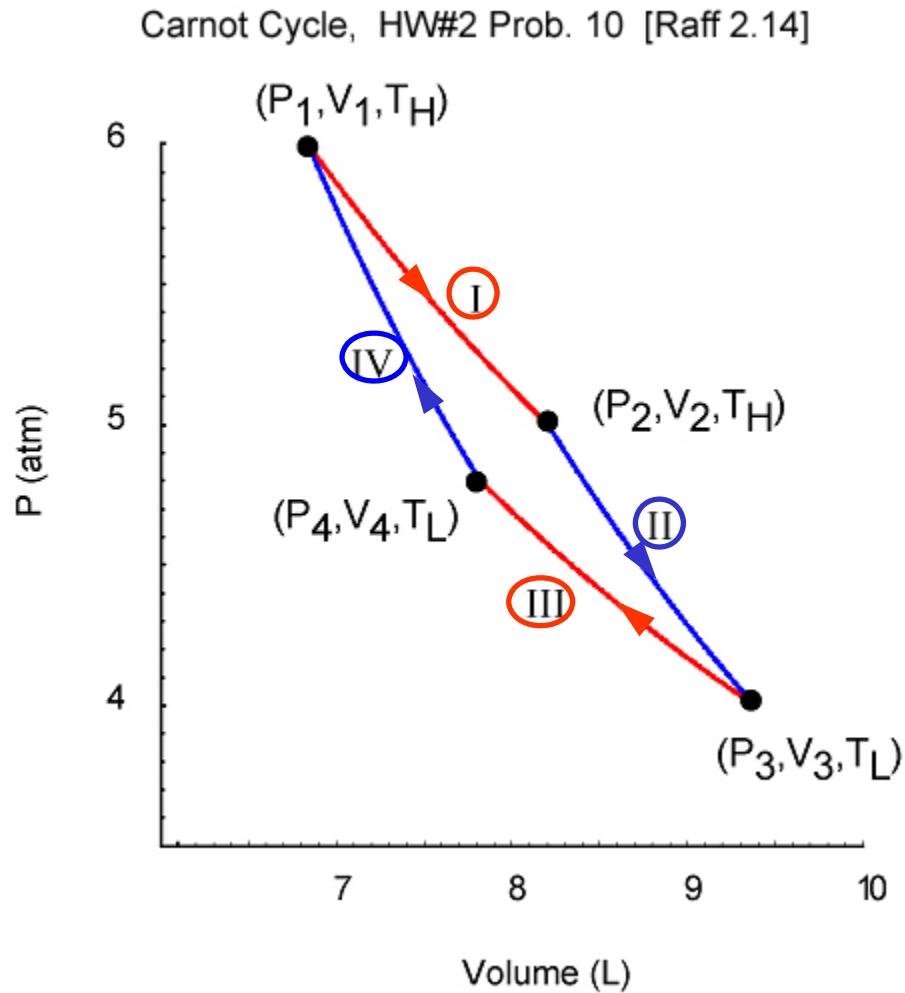
**STEP 2:** After completion of STEP 1, the gas is expanded adiabatically and reversibly until the pressure reaches 4 atm.

**STEP 3:** After STEP 2 is completed, the gas is compressed isothermally and reversibly to a final pressure of 4.800 atm.

**STEP 4:** After STEP 3, the gas is compressed adiabatically and reversibly to a pressure of 6 atm, returning the gas to a temperature of 500 K .

- a. Compute  $w$ ,  $q$ , and  $\Delta U$  for STEP 1.
- b. At the completion of STEP 2, what are the temperature and volume of the gas? Compute the amount of work done in STEP 2.
- c. Compute  $w$ ,  $q$ , and  $\Delta U$  for STEP 3.
- d. Compute the amount of work done in STEP 4.
- e. Compute  $w$ ,  $q$ , and  $\Delta U$  for the entire process.

## Problem HW#2 Prob10



### cyclic process

I isothermal expansion

II adiabatic expansion

III isothermal compression

IV adiabatic compression

$$P_1 = 6 \text{ atm}, T_1 = T_H = 500 \text{ K}$$

$$P_2 = 5 \text{ atm}, T_2 = T_H = 500 \text{ K}$$

$$P_3 = 4 \text{ atm}, q_{2 \rightarrow 3} = 0, T_3 = T_L$$

$$P_4 = 4.8 \text{ atm}, T_4 = T_L, q_{4 \rightarrow 1} = 0$$

HINT:  $T_L = 457.3 \text{ K}$