

Chemistry 163B

Lecture 4

Winter 2014

Challenged Penmanship

Notes

1st Law recapitulation

$U \equiv$ internal energy

$$dU_{sys} = \bar{d}q_{sys} + \bar{d}w_{sys} + dn_{sys} \quad (n = \text{number of moles; } dn = 0 \text{ for closed system})$$

$$dU_{sys} = -dU_{surr} \quad (\text{energy conserved})$$

dU is exact differential

U is a state function

completely general

$$dU = \bar{d}q + \bar{d}w_{PV} + \bar{d}w_{other} + dn$$

for only P-V work and closed system ($\bar{d}w_{other} = 0$, $dn = 0$)

$$dU = \bar{d}q - P_{ext} dV$$

- **Constant volume process** $dU_V = \bar{d}q_V$ $\Delta U_V = q_V$
- **Adiabatic process** $dU = \bar{d}w$ $\Delta U = w$

isothermal expansion of ideal gas: concepts illustrated

10 atm
300 K
1 mole

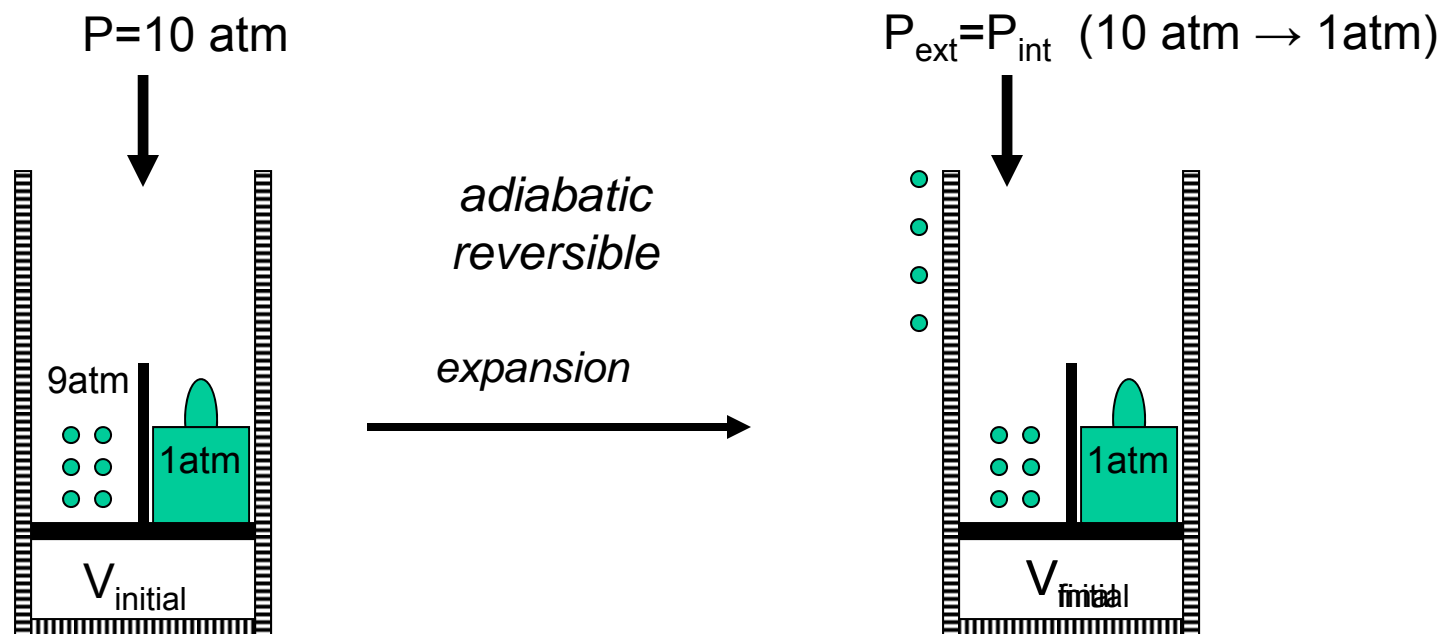


1 atm
300 K
1 mole

	<i>irreversible</i> $P_{\text{ext}} = \text{const}$	<i>reversible</i> $P_{\text{ext}} = P_{\text{int}} = P$
isothermal expansion	$\Delta V > 0, \Delta T = 0, \Delta U = 0, q = -w$	$\Delta V > 0, \Delta T = 0, \Delta U = 0, q = -w$
ΔU	<u>0</u>	<u>0</u>
<u>$w = -\int P_{\text{ext}} dV$</u>	$w = -P_{\text{ext}} (V_{\text{final}} - V_{\text{initial}})$ $= -nRT P_{\text{ext}} \left(\frac{1}{P_{\text{final}}} - \frac{1}{P_{\text{initial}}} \right)$ $= \underline{-2244 \text{ J}}$	$w = -nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}}$ $= +nRT \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$ $= \underline{-5743 \text{ J}}$
$q = -w$	<u>$q = 2244 \text{ J}$</u>	<u>$q = 5743 \text{ J}$</u>

- $\Delta U_{\text{irrev}} = \Delta U_{\text{rev}}$
- $\Delta V > 0, w < 0$ work is done ON
- $q_{\text{irrev}} \neq q_{\text{rev}}$
- $w_{\text{irrev}} \neq w_{\text{rev}}$
- $-(-5743 \text{ J}) > -(-2244 \text{ J})$

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

two relationships for ideal gasses: a (μ sec) look ahead
(will prove rigorously in next lecture)

- for any substance

$$dU_V = \delta q_V = n \bar{C}_V dT \quad \text{and} \quad \Delta U_V = \int n \bar{C}_V dT \quad \text{for a constant volume process}$$

- but for an ideal gas

$$dU = n \bar{C}_V dT \quad \text{and} \quad \Delta U = n \bar{C}_V \Delta T \quad \text{for ANY path (not only constant V process)}$$

[other parts of path, changes of P and V with constant T, give zero contribution to ΔU]

- for ideal gas

$$\bar{C}_P = \bar{C}_V + R$$

- monatomic ideal gas

$$\bar{C}_V = \frac{3}{2} R \quad \bar{C}_P = \frac{5}{2} R$$

[simple proof coming soon]

adiabatic processes and the First Law

$$q = 0$$

$$\Delta U = w$$

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

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

work

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

reversible

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

ideal gas

so as before ??:

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

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



but T varies along
path initial → final

for a reversible adiabatic expansion of ideal gas

important derivation (next few slides):

for reversible adiabatic expansion of ideal gas

relate (P,V,T) at any point along the
reversible adiabatic path to
(P_{initial} , V_{initial}, T_{initial})

STRATEGY: $\underline{dU_{adiabatic}} = \underline{\delta w} = -PdV = n\bar{C}_V dT = \underline{dU_{ideal\ gas}}$

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

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

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

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

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

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

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

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**

know: $T_{\text{initial}}, V_{\text{initial}}, V_{\text{final}} \rightarrow$ calculate T_{final}
 $T_{\text{initial}}, V_{\text{initial}}, T_{\text{final}} \rightarrow$ calculate V_{final}

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

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

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

know: $T_{\text{initial}}, P_{\text{initial}}, P_{\text{final}} \rightarrow$ calculate T_{final}

summarizing (and HW3 #15)

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

and

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

and

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

where $\gamma = \frac{\bar{C}_P}{\bar{C}_V}$

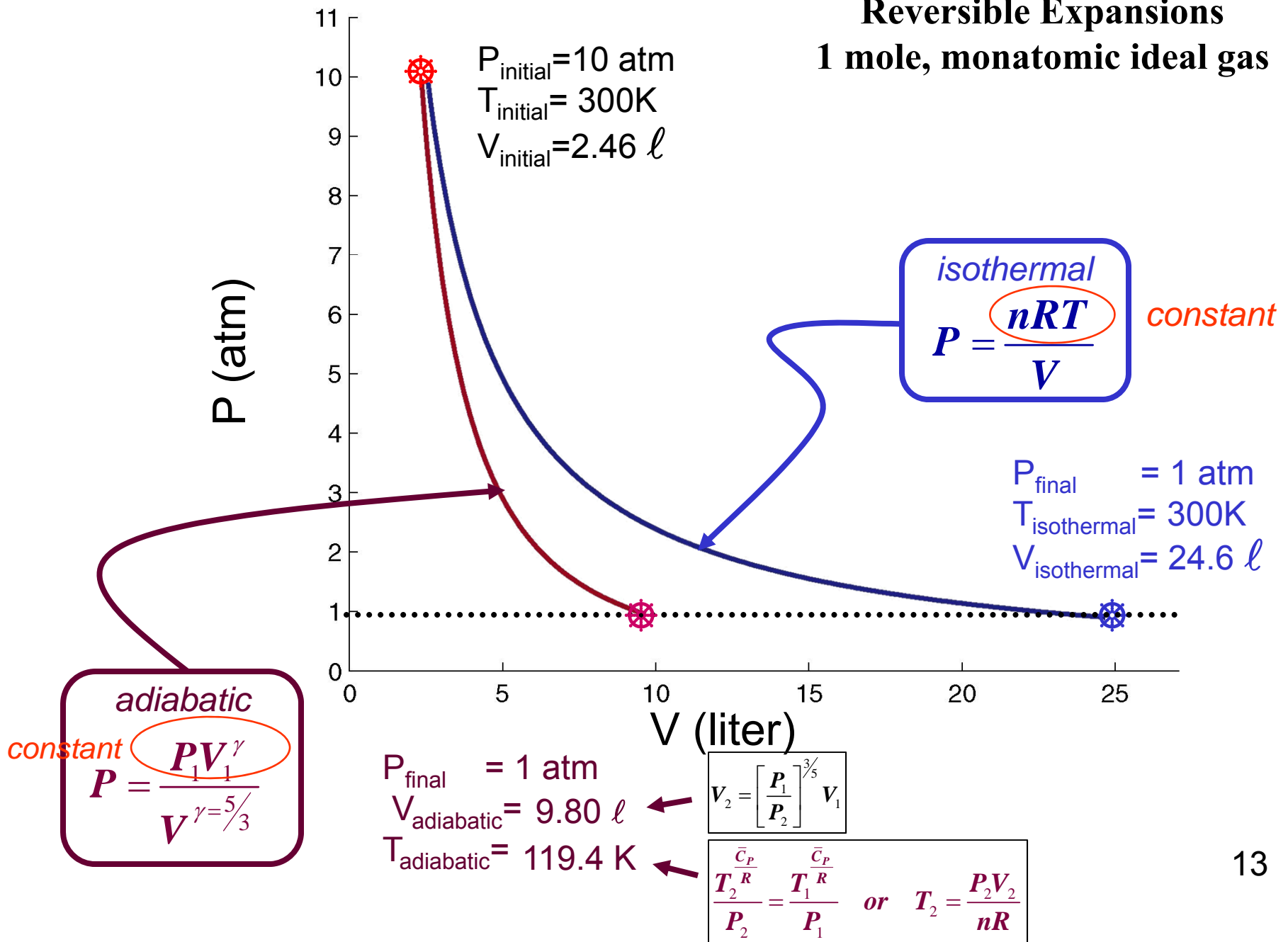
T_VS_V

T_VS_P

P_VS_V

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**

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

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

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

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

calc

ΔU

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

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

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

calc

q, w

$$q = 0$$

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

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

HW#2 Problem 10 (Raff 2.14)

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.

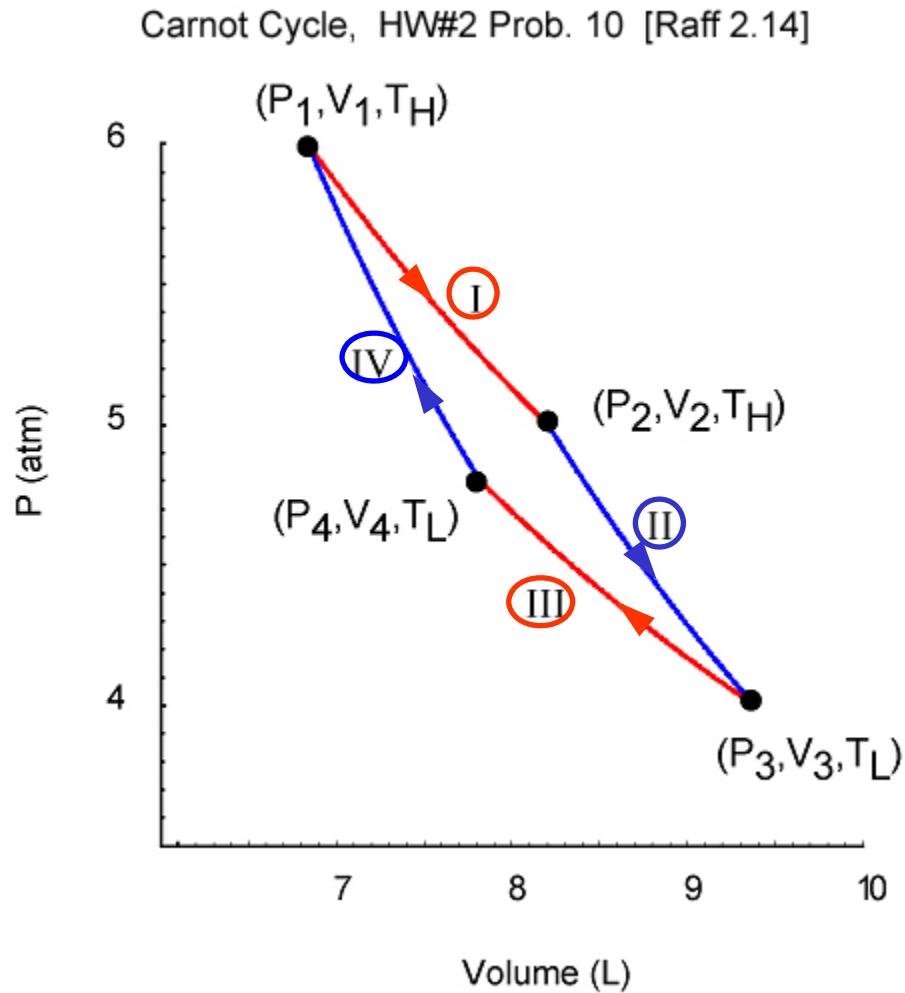
STEP 2: After completion of STEP 1, the gas is expanded adiabatically and reversibly until the pressure reaches 4 atm.

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 ΔU 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 ΔU for STEP 3.
- d. Compute the amount of work done in STEP 4.
- e. Compute w , q , and ΔU 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: $T_L = 457.3 \text{ K}$

lectures this Wednesday-Friday [3X]
*(Monday 20th Jan **HOLIDAY**; exam Friday, 31st Jan)*



better make it a triple