

Chemistry 163B

Lecture 4

1st Law Calculations for Ideal Gases

Winter 2020

Challenged Penmanship

Notes

Menu: for TODAY(s)



- **Review of equivalent statements of 1st Law**
- **Ideal gas calculations for REVERSIBLE adiabatic expansion**
(fourth condition, viz lectures 2-3, slide #13)
- **P, V, T constraints for reversible expansion ideal gas**
(HW#2 15)
- **Cyclic path: combination of reversible adiabatic and isothermal expansions/compressions** *(HW#2 10, HELLO CARNOT CYCLE !!)*

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

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

- $\Delta U_{\text{irrev}} = \Delta U_{\text{rev}}$?? what can one say about the function U
- $\Delta V > 0, w < 0$ work is done ON ?? ON system or ON surroundings
- $q_{\text{irrev}} \neq q_{\text{rev}}$?? what does this imply about the quantities
- $w_{\text{irrev}} \neq w_{\text{rev}}$ q and w and the differentials dq and dw
- $-(-5743 \text{ J})_{\text{rev}} > -(-2244 \text{ J})_{\text{irrev}}$?? which does more work ON surroundings rev or irrev

two relationships for ideal gasses: a short look ahead

(will prove rigorously in next lecture)

- for any substance (*only P-V work*)

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

- 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, i.e. 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

$$q = 0$$

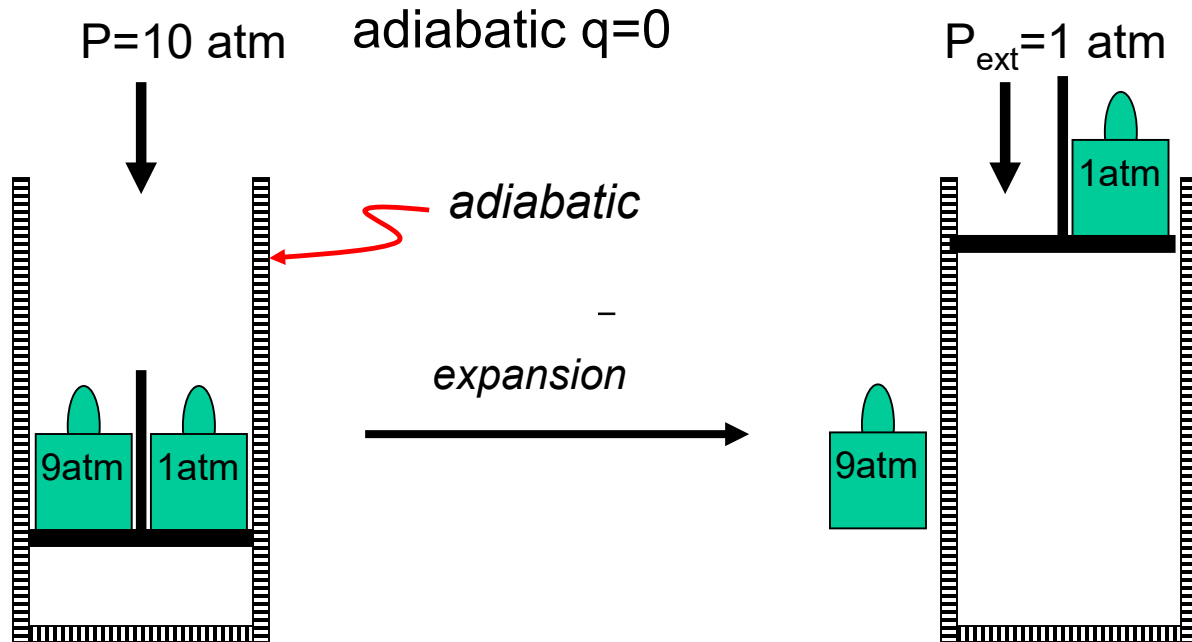
$$\Delta U = w = -\int P_{ext} dV \quad \text{general}$$

$$\Delta U = n\bar{C}_V \Delta T \quad \text{ideal gas}$$

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

Pressure-Volume work: irreversible adiabatic expansion $P_{\text{ext}} = \text{constant}$



adiabatic expansion against constant pressure (irreversible)

1 mole
300K
10 atm
 V_1

$$\Delta U = 0 + w = -P_{\text{ext}}(V_2 - V_1) = -1 \text{ atm} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

Will soon show holds for ideal gas $\Delta U = n\bar{C}_V\Delta T = \frac{3}{2}nR(T_2 - T_1)$
V NOT const

$$-1 \text{ atm} (1 \text{ mol}) R \left(\frac{T_2}{1 \text{ atm}} - \frac{300 \text{ K}}{10 \text{ atm}} \right) = \frac{3}{2} (1 \text{ mol}) R (T_2 - 300 \text{ K})$$

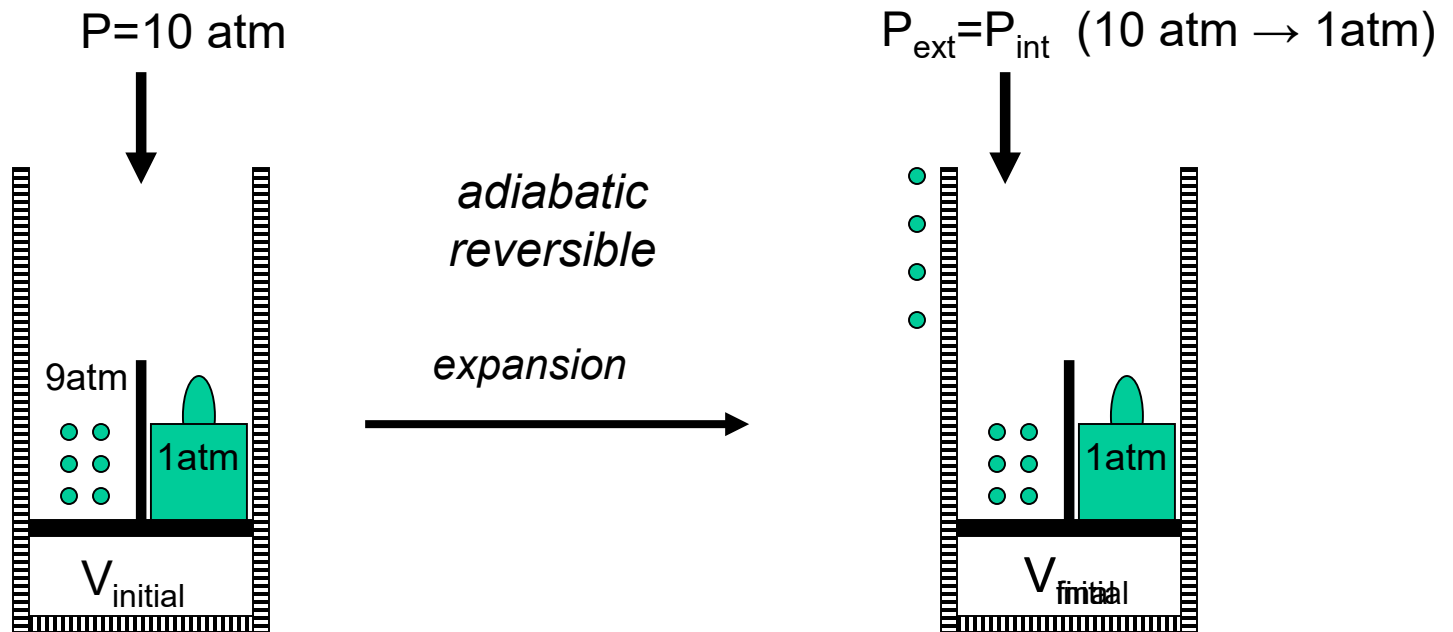
1 mole
 $T_2 ? \text{ K}$
1 atm
 V_2



$T_2 = 192 \text{ K}$ $w = -1347 \text{ J} = -1.347 \text{ kJ}$

no q in, less work done than isothermal (-2.244 kJ)

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

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 \rightarrow final

for a reversible adiabatic expansion of ideal gas

important derivation (next few slides):

for reversible adiabatic expansion of ideal gas

want to relate (P,V,T) at any point along the
reversible adiabatic path to

(P_{initial} , V_{initial} , T_{initial})

HW2 #15

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

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 HW2 #15)

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

and

$$\frac{\bar{C}_P}{P_2} = \frac{\bar{C}_P}{P_1}$$

and

HW2 #15 → $P_1 V_1^\gamma = P_2 V_2^\gamma$ 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

adiabatic reversible expansion: $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$ what's T_f ??

EXAMPLE YEA !

$P_1=10 \text{ atm}$
 $T_1=300\text{K}$
 $V_1=2.462 \text{ l}$
 $n=1 \text{ mol}$



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

use T vs P

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

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

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

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

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

adiabatic reversible expansion: $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$ what's V_f ??

ANOTHER EXAMPLE DOUBLE YEA ! YEA !!

$P_1= 10 \text{ atm}$
 $T_1= 300\text{K}$
 $V_1=2.462 \ell$
 $n=1$

\longrightarrow $P_2= 1 \text{ atm}$
 $V_2= ???$

use **P vs V** $P_1V_1^\gamma = P_2V_2^\gamma$

$$P_2V_2^\gamma = P_1V_1^\gamma \quad \gamma = \frac{\bar{C}_P}{\bar{C}_V} = \frac{5/2 R}{3/2 R} = \frac{5}{3}$$

$$V_2 = V_1 \left(\frac{P_1}{P_2} \right)^{\frac{1}{\gamma}} = V_1 \left(\frac{P_1}{P_2} \right)^{\frac{3}{5}}$$

$$V_2 = V_1 \left(\frac{10 \text{ atm}}{1 \text{ atm}} \right)^{\frac{3}{5}} = 2.46 \ell \times (10)^{\frac{3}{5}}$$

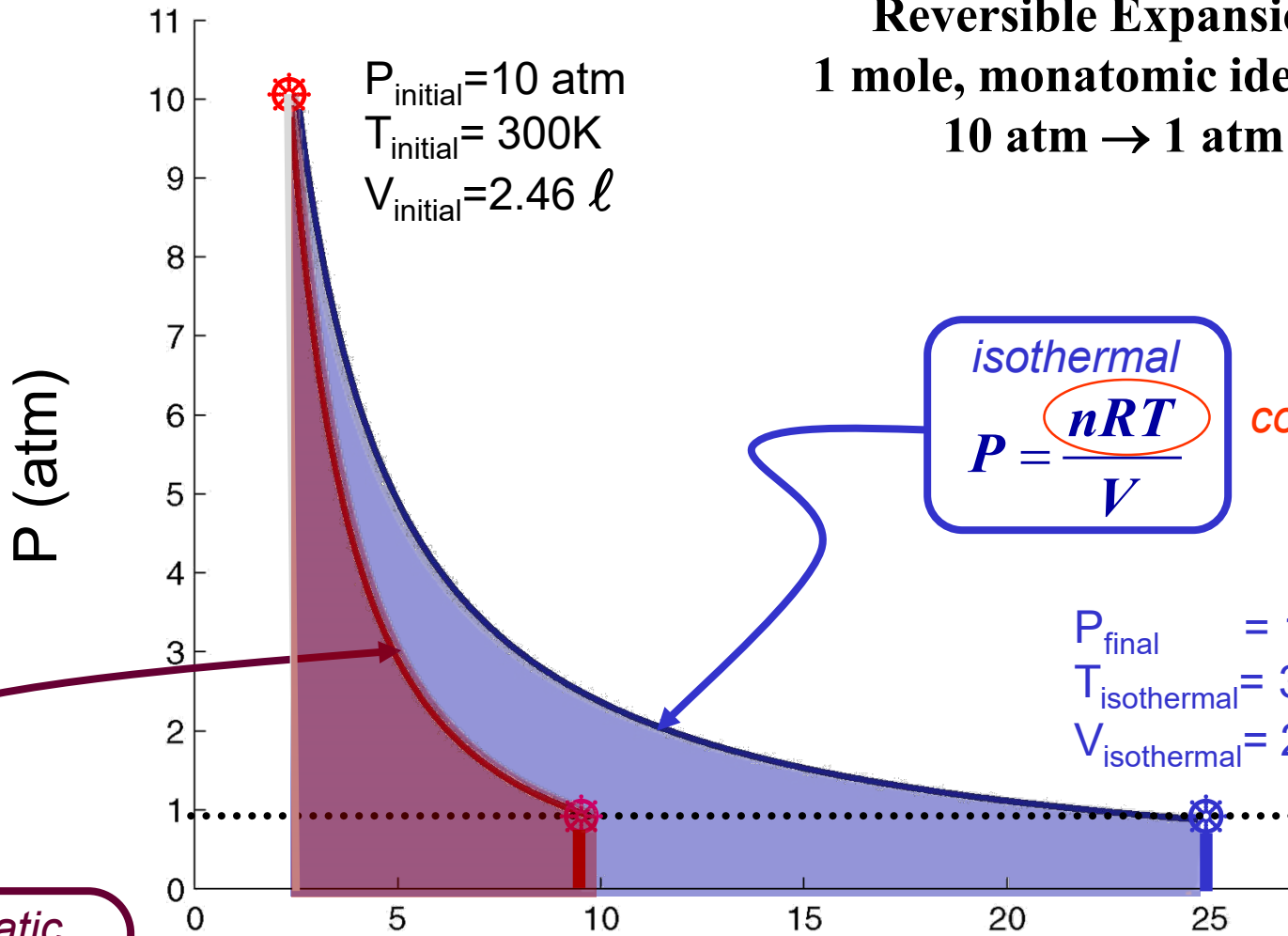
$V_2 = 2.462 \ell \times (3.98) = 9.80 \ell$

also:

$$V_2 = \frac{nRT_2}{P_2}$$
$$V_2 = \frac{1 \text{ mol} (.0821 \ell \text{ atm mol}^{-1} \text{ K}^{-1})(119.4 \text{ K})}{1 \text{ atm}}$$
$$V_2 = 9.80 \ell$$

Reversible Expansions

1 mole, monatomic ideal gas
10 atm → 1 atm



$P_{\text{initial}} = 10 \text{ atm}$
 $T_{\text{initial}} = 300 \text{ K}$
 $V_{\text{initial}} = 2.46 \text{ l}$

isothermal

$$P = \frac{nRT}{V} \quad \text{constant}$$

$P_{\text{final}} = 1 \text{ atm}$
 $T_{\text{isothermal}} = 300 \text{ K}$
 $V_{\text{isothermal}} = 24.6 \text{ l}$

adiabatic

$$P = \frac{P_1 V_1^\gamma}{V^\gamma} \quad \text{constant}$$

$P_{\text{final}} = 1 \text{ atm}$
 $V_{\text{adiabatic}} = 9.80 \text{ l}$
 $T_{\text{adiabatic}} = 119.4 \text{ K}$

$$V_2 = \left[\frac{P_1}{P_2} \right]^{3/5} V_1$$

$$\frac{\bar{c}_P T_2^R}{P_2} = \frac{\bar{c}_P T_1^R}{P_1} \quad \text{or} \quad T_2 = \frac{P_2 V_2}{nR}$$

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

calc
 ΔU

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

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

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

calc
q,w

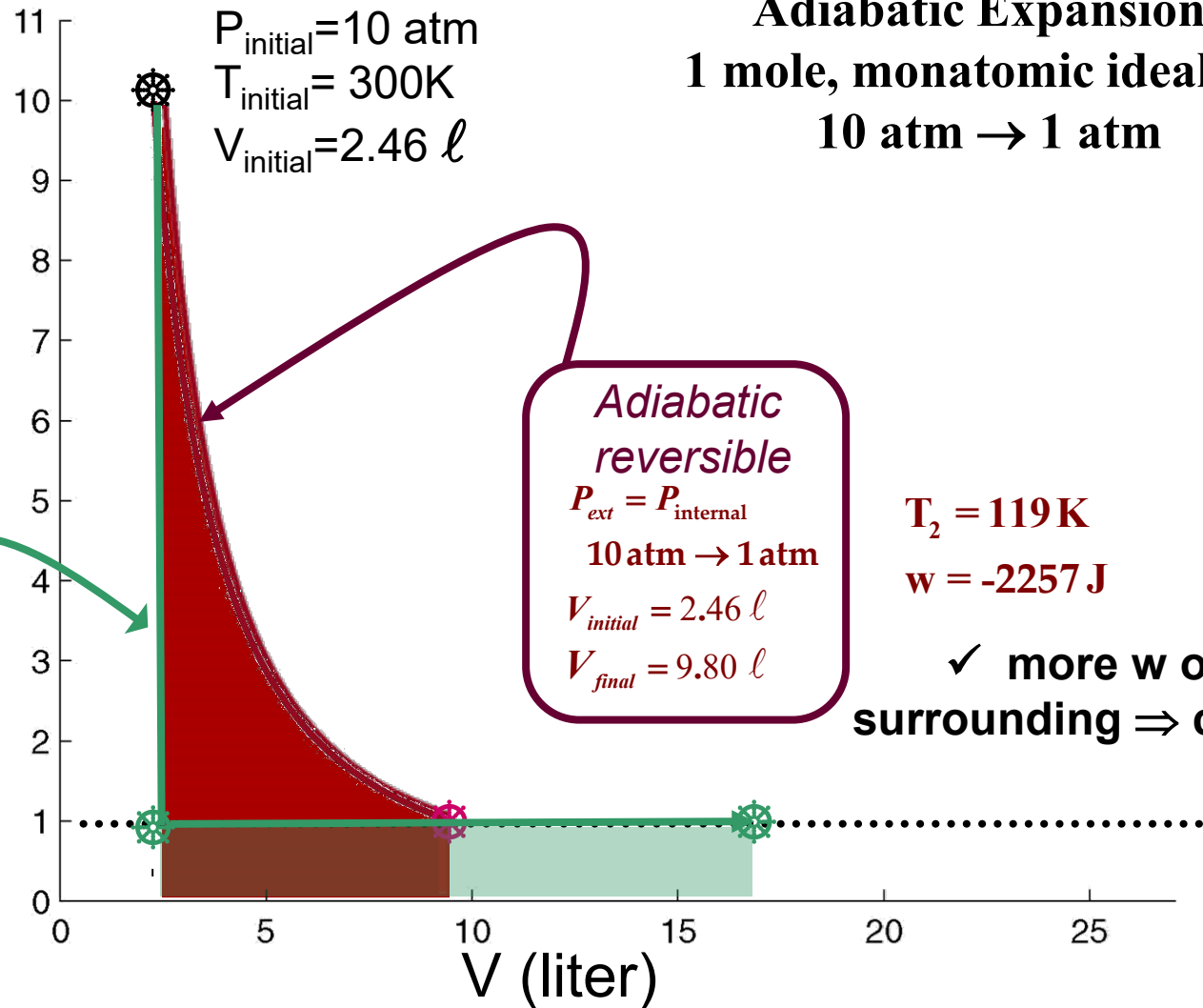
$$q = 0$$

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

vs -5.743 kJ for isothermal reversible
10 atm \rightarrow 1 atm at 300K

Adiabatic Expansions

1 mole, monatomic ideal gas
10 atm → 1 atm



$T_2 = 119 \text{ K}$
 $w = -2257 \text{ J}$

✓ more w on surrounding ⇒ cooler

$T_2 = 192 \text{ K}$
 $w = -1347 \text{ J}$

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.

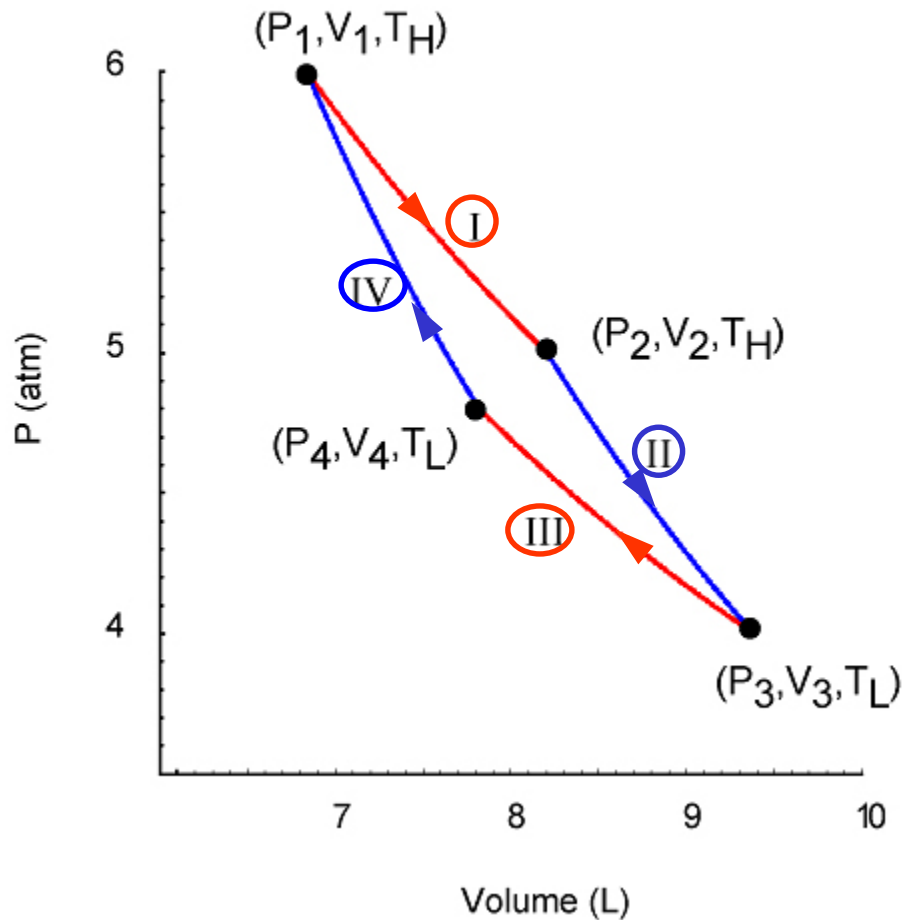
STEP 3: After STEP 2 is completed, the gas is compressed isothermally and reversibly to a final pressure of 4.800 atm.

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 .

- Compute w , q , and ΔU for STEP 1.
- At the completion of STEP 2, what are the temperature and volume of the gas? Compute the amount of work done in STEP 2.
- Compute w , q , and ΔU for STEP 3.
- Compute the amount of work done in STEP 4.
- Compute w , q , and ΔU for the entire process.

Problem HW#2 Prob10

Carnot Cycle, HW#2 Prob. 10 [Raff 2.14]



cyclic process

- I isothermal expansion
- II adiabatic expansion
- III isothermal compression
- IV adiabatic compression

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

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

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

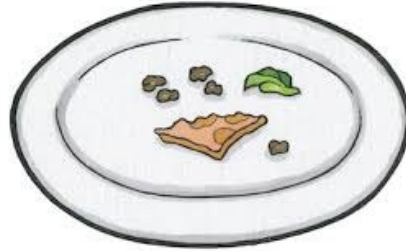
$$P_4 = 4.8 \text{ atm}, T_4 = T_L, q_{4 \rightarrow 1} = 0$$

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



*I*deal Gas Calculations and the *f*irst *L*aw 'four paths to enlightenment'

handout # 10 provides a summary of
our work on calculations and
interpretations for ideal gas
expansions and compressions



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- ✓ **Review of equivalent statements of 1st Law**
- ✓ **Ideal gas calculations for REVERSIBLE adiabatic expansion**
(fourth condition, viz lectures 2-3, slide #13)
- ✓ **P, V, T constraints for reversible expansion ideal gas**
(HW#2 15)
- ✓ **Cyclic path: combination of reversible adiabatic and isothermal expansions/compressions** *(HW#2 10, HELLO CARNOT CYCLE !!)*

End of Lecture 4