# Chemistry 163B Winter 2020
# notes for lecture 4- First Law Calculations

Chemistry 163B

Lecture 4

1st Law Calculations for Ideal Gases

Winter 2020

Challenged Penmanship

Notes

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***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 !!)*

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***1st Law recapitulation***

U ≡ internal energy

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

$dU_{sys} = -dU_{surr}$ *(energy conserved)*

*dU is exact differential*

*U is a state function* *completely general*

$$dU = \text{đ}q + \text{đ}w_{PV} + \text{đ}w_{other} + dn$$

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

$$dU = \text{đ}q - P_{ext}dV$$

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

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***isothermal expansion of ideal gas: concepts illustrated***

10 atm
300 K
1 mole

⇩

1 atm
300 K
1 mole

| | ***irreversible*** $P_{ext}$=const | ***reversible*** $P_{ext}=P_{int}=P$ |
|---|---|---|
| isothermal expansion | ΔV>0, ΔT=0, ΔU=0, q=-w | ΔV>0, ΔT=0, ΔU=0, q=-w |
| **ΔU** | **0** | **0** |
| $w = -\int P_{ext}dV$ | $w = -P_{ext}(V_{final} - V_{initial})$ $= -nRTP_{ext}\left(\frac{1}{P_{final}} - \frac{1}{P_{initial}}\right)$ $= -2244\text{ J}$ | $w = -nRT\ln\frac{V_{final}}{V_{initial}}$ $= +nRT\ln\frac{P_{final}}{P_{initial}}$ $= -5743\text{ J}$ |
| q=−w | q =2244 J | q =5743 J |

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

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

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

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

- but for an ideal gas

$dU = n\bar{C}_V dT$ **and** $\Delta U = n\bar{C}_V \Delta T$ **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]*

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***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 ΔV > 0** $-\int PdV = w < 0$ **ΔU < 0 (ideal gas) system cools**

**compression ΔV < 0** $-\int PdV = w > 0$ **ΔU > 0 (ideal gas) system warms**

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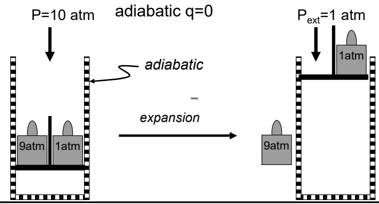
# notes for lecture 4- First Law Calculations

### *Pressure-Volume work: irreversible adiabatic expansion $P_{ext}$ = constant*

P=10 atm adiabatic q=0 $P_{ext}$=1 atm




*adiabatic expansion against constant pressure (irreversible)*

1mole
300K
10 atm
$V_1$

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

Will soon show holds for ideal gas V **NOT** const

$$\Delta U = n\bar{C}_V \Delta T = \frac{3}{2}nR(T_2 - T_1)$$

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

1mole
$T_2$ ? K
1 atm
$V_2$

brr! $T_2 = 192\,K$ $w = -1347\,J = -1.347\,kJ$ **no q in, less work done than isothermal** ***(-2.244 kJ)***

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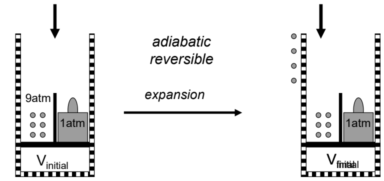
### *Pressure-Volume work* ***reversible*** *adiabatic expansion*

P=10 atm $P_{ext}=P_{int}$ (10 atm → 1atm)




- q=0
- w= - ∫ $P_{ext}dV$
- ΔU=q+w
- ΔV > 0 ⇨ w < 0 ($w_{surr}$ > 0)
- ΔU= w < 0 ⇨ gas cools as V increases

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### *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 ??:

$$w = -\int_{initial}^{final} \frac{nRT}{V}\,dV \;\cancel{=}\; -nRT\int_{initial}^{final}\frac{dV}{V}$$

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


but T varies along path initial → final

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### *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:** $dU_{adiabatic} = đw = -PdV$ **=** $n\bar{C}_V dT = dU_{ideal\ gas}$

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

$$dU = đw = -PdV$$

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

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

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

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

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

*or*

$$\frac{\bar{C}_V}{R}\ln\frac{T_2}{T1} = -\ln\frac{V_2}{V_1} = \ln\frac{V_1}{V_2}$$

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### *for adiabatic, reversible, ideal gas: TvsV* $\left(\frac{T_2}{T_1}\right)^{\bar{C}_V/R} = \left(\frac{V_1}{V_2}\right)$

$$\frac{\bar{C}_V}{R}\ln\frac{T_2}{T1} = \ln\frac{V_1}{V_2}$$

$$\ln\left(\frac{T_2}{T1}\right)^{\frac{\bar{C}_V}{R}} = \ln\frac{V_1}{V_2}$$

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

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

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

know: $T_{initial}$, $V_{initial}$, $V_{final}$ ➔ calculate $T_{final}$
$T_{initial}$, $V_{initial}$, $T_{final}$ ➔ calculate $V_{final}$

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# notes for lecture 4- First Law Calculations

***(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*

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

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

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

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

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

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

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

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

know: $T_{initial}$, $P_{initial}$, $P_{final}$ ➔ calculate $T_{final}$

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***summarizing (and HW2 #15)***

$$\boxed{T_2^{\frac{\bar{C}_V}{R}} V_2 = T_1^{\frac{\bar{C}_V}{R}} V_1}$$ ***T** vs **V***

*and*

$$\boxed{\frac{T_2^{\frac{\bar{C}_P}{R}}}{P_2} = \frac{T_1^{\frac{\bar{C}_P}{R}}}{P_1}}$$ ***T** vs **P***

*and*

HW2 #15 ⟶ $$\boxed{P_1 V_1^{\gamma} = P_2 V_2^{\gamma}} \ where \ \gamma = \frac{\bar{C}_P}{\bar{C}_V}$$ ***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**

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***adiabatic reversible** expansion: $P_1$=10 atm → $P_2$=1 atm what's $T_f$??*

**EXAMPLE YEA !**

**$P_1$= 10 atm**
**$T_1$= 300K** ⟶ **$P_2$= 1 atm**
**$V_1$=2.462 ℓ** **$T_2$= ???**
**n=1 mol**

use **T** vs **P** $\frac{T_2^{\frac{\bar{C}_P}{R}}}{P_2} = \frac{T_1^{\frac{\bar{C}_P}{R}}}{P_1}$

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

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

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

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

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***adiabatic reversible** expansion: $P_1$=10 atm → $P_2$=1 atm what's $V_f$??*

**ANOTHER EXAMPLE DOUBLE YEA ! YEA !!**

**$P_1$= 10 atm**
**$T_1$= 300K** ⟶ **$P_2$= 1 atm**
**$V_1$=2.462 ℓ** **$V_2$= ???**
**n=1**

use **P** vs **V** $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma} \qquad \gamma = \frac{\bar{C}_P}{\bar{C}_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

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

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

$$\boxed{V_2 = 2.462\ell \times (3.98) = 9.80\ell}$$

also:

$$V_2 = \frac{nRT_2}{P_2}$$

$$V_2 = \frac{1\,mol(.0821\ell\ atm\ mol^{-1}K^{-1})(119.4K)}{1atm}$$

$$V_2 = 9.80\ell$$

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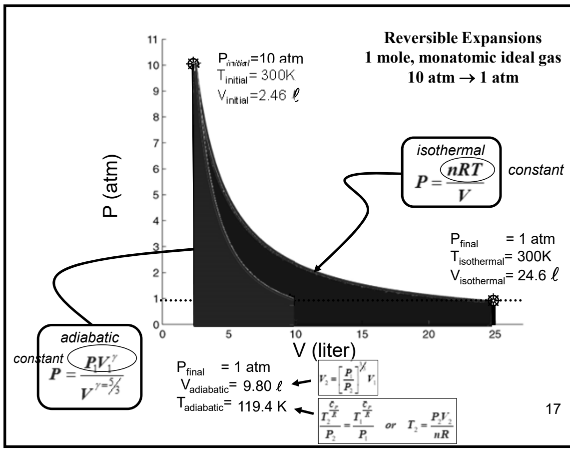


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***adiabatic** reversible expansion: $P_1$=10 atm → $P_2$=1 atm*

calc ΔU

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

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

$$\boxed{\Delta U = \textbf{-2.257 kJ}}$$

calc q,w

$$q = 0$$

$$q + w = \Delta U \Rightarrow w = \textbf{–2.257 kJ}$$

*vs -5.743 kJ for isothermal reversible 10 atm → 1 atm at 300K*

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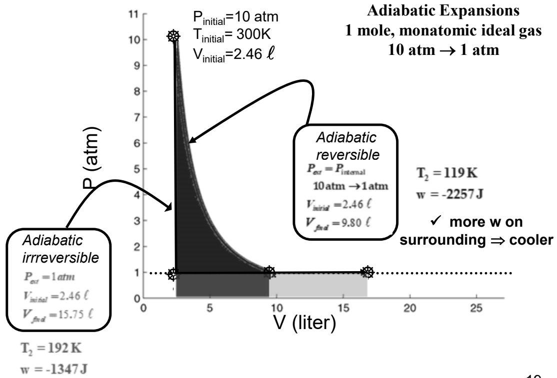





## *HW#2 Problem 10 (Raff 2.14)*

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.

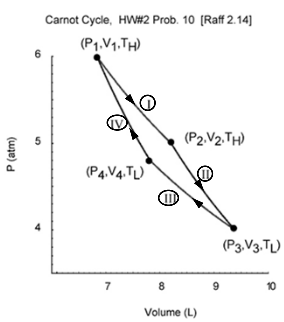
**STEP 3:** After STEP 2 is completed, the gas is compressed isothermally and reversibly to a final pressure of 4.800 atm.

**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

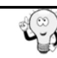
$P_1$=6 atm, $T_1=T_H$=500K
$P_2$=5 atm, $T_2=T_H$=500K
$P_3$=4 atm, $q_{2\to3}$ = 0, $T_3=T_L$
$P_4$=4.8 atm, $T_4=T_L$, $q_{4\to1}$= 0

HINT: $T_L$=457.3K



## *You've Made IT*





**Ideal Gas Calculations and the First Law 'four paths to enlightenment'**

**<u>handout # 10</u> provides a summary of our work on calculations and interpretations for ideal gas expansions and compressions**



## *Menu: for TODAY(s)* DONE !!

- ✓ **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