


# Chemistry 163B Winter 2020

## notes for lecture 4- First Law Calculations

Chemistry 163B  
Lecture 4  
1<sup>st</sup> Law Calculations for Ideal Gases  
Winter 2020  
Challenged Penmanship  
Notes

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Menu: for TODAY(s)



- Review of equivalent statements of 1<sup>st</sup> 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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1<sup>st</sup> Law recapitulation

U ≡ internal energy  
 $dU_{sys} = \delta q_{sys} + \delta w_{sys} + dn_{sys}$  (n=number of moles; dn=0 for closed system)  
 $dU_{sys} = -dU_{sur}$  (energy conserved)  
 dU is exact differential  
 U is a state function completely general

$dU = \delta q + \delta w_{PV} + \delta w_{other} + dn$   
 for only P-V work and closed system ( $\delta w_{other} = 0, dn=0$ )  
 $dU = \delta q - P_{ext}dV$

- Constant volume process  $dU_V = \delta q_V, \Delta U_V = q_V$
- Adiabatic process  $dU = \delta w, \Delta U = w$

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isothermal expansion of ideal gas: concepts illustrated

	irreversible $P_{ext} = \text{const}$	reversible $P_{ext} = P_{int} = P$
10 atm 300 K 1 mole	isothermal expansion $\Delta V > 0, \Delta T = 0, \Delta U = 0, q = -w$	isothermal expansion $\Delta V > 0, \Delta T = 0, \Delta U = 0, q = -w$
↓	$\Delta U = 0$	$\Delta U = 0$
1 atm 300 K 1 mole	$w = -\int P_{ext}dV$ $w = -P_{ext}(V_{final} - V_{initial})$ $= -nRT P_{ext} \left( \frac{1}{P_{final}} - \frac{1}{P_{initial}} \right)$ $= -2244 \text{ J}$	$w = -nRT \ln \frac{V_{final}}{V_{initial}}$ $= +nRT \ln \frac{P_{final}}{P_{initial}}$ $= -5743 \text{ J}$
	$q = -w$	$q = 5743 \text{ J}$

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

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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)  
 $dU_V = \delta q_V = n\bar{C}_V dT$  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  $\Delta U$ ]

- for ideal gas  
 $\bar{C}_P = \bar{C}_V + R$
- monatomic ideal gas  
 $\bar{C}_V = \frac{3}{2}R, \bar{C}_P = \frac{5}{2}R$   
[simple proof coming soon]

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adiabatic processes and the First Law

$q = 0$   
 $\Delta U = w = -\int P_{ext}dV$  general

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

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

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

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

**adiabatic expansion against constant pressure (irreversible)**

<p>1 mole 300K 10 atm <math>V_1</math></p>	<p><math>\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)</math></p> <p><small>Will soon show holds for ideal gas</small>  <math>\Delta U = n\bar{C}_v \Delta T = \frac{3}{2} nR(T_2 - T_1)</math></p> <p><math>-1 \text{ atm} (10 \text{ atm}) R \left( \frac{T_2}{1 \text{ atm}} - \frac{300 \text{ K}}{10 \text{ atm}} \right) = \frac{3}{2} (1 \text{ mole}) R (T_2 - 300 \text{ K})</math></p>	<p>1 mole <math>T_2</math> ? K 1 atm <math>V_2</math></p>
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brr!  $T_2 = 192 \text{ K}$      $w = -1347 \text{ J} = -1.347 \text{ kJ}$     no q in, less work done than isothermal (-2.244 kJ)    7

**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

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**ideal gas adiabatic reversible processes WORK**

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

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

$$P = \frac{nRT}{V} \quad \text{ideal gas}$$

so as before ??:

$$w = - \int_{\text{initial}}^{\text{final}} \frac{nR(T)}{V} dV \quad \text{DUH!}$$

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

but T varies along path initial  $\rightarrow$  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  
 $(P_{\text{initial}}, V_{\text{initial}}, T_{\text{initial}})$     HW2 #15

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

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

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

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

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

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

$$\int_{T_1}^{T_2} \frac{\bar{C}_v}{R} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{dV}{V}$$

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

or

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

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for adiabatic, reversible, ideal gas:  $TvsV \quad \left( \frac{T_2}{T_1} \right)^{\bar{C}_v} = \left( \frac{V_1}{V_2} \right)$

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

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

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

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

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

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(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

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

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

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

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

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

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

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

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

know:  $T_{\text{initial}}, P_{\text{initial}}, P_{\text{final}} \rightarrow$  calculate  $T_{\text{final}}$  13

summarizing (and HW2 #15)

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

and

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

and

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

HW2 #15  $\rightarrow$

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

T vs V  
T vs P  
P vs V

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

EXAMPLE YEA!

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

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

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

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

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

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

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

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

ANOTHER EXAMPLE DOUBLE YEA! YEA!!

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

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

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

$$P_2 V_2^\gamma = P_1 V_1^\gamma \quad \gamma = \frac{\bar{C}_p}{\bar{C}_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

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

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

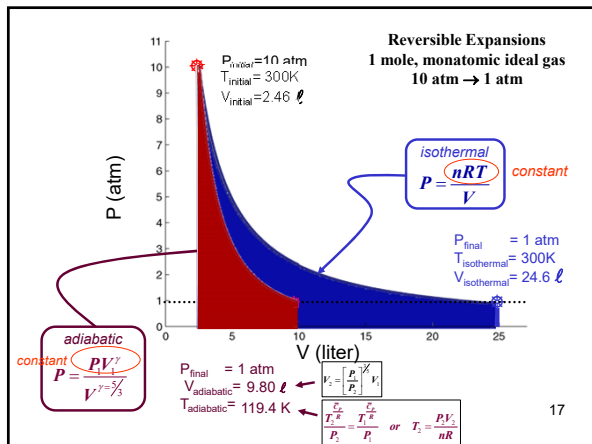
$$V_2 = 2.462 \text{ l} \times (3.98) = 9.80 \text{ l}$$

also:

$$V_2 = \frac{nRT_2}{P_2} = \frac{1 \text{ mol} (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (119.4 \text{ K})}{1 \text{ atm}}$$

$$V_2 = 9.80 \text{ l}$$

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

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

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

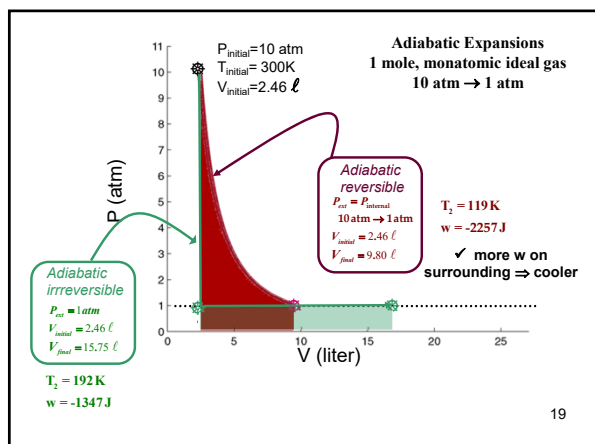
calc  $q + w = \Delta U \Rightarrow q = 0 \Rightarrow w = -2.257 \text{ kJ}$

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

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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 5 atm.

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.

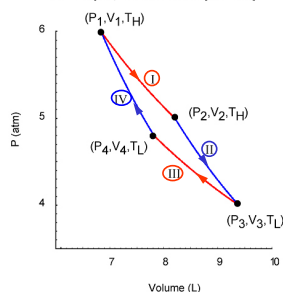
STEP 4: After STEP 3, the gas is compressed adiabatically and reversibly to a pressure of 6 atm, returning the gas to a temperature of 500 K.

- Compute  $w$ ,  $q$ , and  $\Delta U$  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  $\Delta U$  for STEP 3.
- Compute the amount of work done in STEP 4.
- Compute  $w$ ,  $q$ , and  $\Delta U$  for the entire process.

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### Problem HW#2 Prob10

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



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### You've Made IT



## Ideal Gas Calculations and the First Law '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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Menu: for TODAY(s)

**DONE !!**



- ✓ Review of equivalent statements of 1<sup>st</sup> 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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End of Lecture 4

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