

# Chemistry 163B Winter 2014

## notes for lecture 4

Chemistry 163B  
Lecture 4  
Winter 2014  
Challenged Penmanship  
Notes

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### 1<sup>st</sup> Law recapitulation

$U \equiv$  internal energy

$dU_{sys} = dq_{sys} + dw_{sys} + dn_{sys}$  ( $n$ =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

$dU = dq + dw_{PV} + dw_{other} + dn$

for only P-V work and closed system ( $dw_{other} = 0, dn=0$ )

$dU = dq - P_{ext}dV$

- Constant volume process  $dU_v = \bar{c}_v dT_v$      $\Delta U_v = q_v$
- Adiabatic process  $dU = \bar{c}_v dT$      $\Delta U = w$

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### isothermal expansion of ideal gas: concepts illustrated

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

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

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### Pressure-Volume work reversible adiabatic expansion

$P = 10 \text{ atm}$        $P_{ext} = P_{int} (10 \text{ atm} \rightarrow 1 \text{ atm})$

adiabatic reversible expansion

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

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### two relationships for ideal gasses: a ( $\mu$ sec) look ahead

*(will prove rigorously in next lecture)*

- for any substance  
 $dU_v = dq_v = n \bar{c}_v dT$  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, 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

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

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

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

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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 ??:

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

DUH!

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

relate (P,V,T) at any point along the reversible adiabatic path to (P<sub>initial</sub>, V<sub>initial</sub>, T<sub>initial</sub>)

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<sub>ext</sub>=P<sub>int</sub>=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**  $\left(\frac{T}{V}\right)^{\frac{\bar{C}_V}{R}} = \left(\frac{V}{V}\right)$

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

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

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

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

for any two states (T<sub>1</sub>, V<sub>1</sub>, P<sub>1</sub>) and (T<sub>2</sub>, V<sub>2</sub>, P<sub>2</sub>) along an adiabatic reversible path

know: T<sub>initial</sub>, V<sub>initial</sub>, V<sub>final</sub>  $\rightarrow$  calculate T<sub>final</sub>  
 T<sub>initial</sub>, V<sub>initial</sub>, T<sub>final</sub>  $\rightarrow$  calculate V<sub>final</sub>

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**(other) TvsP 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<sub>1</sub>, V<sub>1</sub>, P<sub>1</sub>) and (T<sub>2</sub>, V<sub>2</sub>, P<sub>2</sub>) along an adiabatic reversible path

know: T<sub>initial</sub>, P<sub>initial</sub>, P<sub>final</sub>  $\rightarrow$  calculate T<sub>final</sub>

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**summarizing (and HW3 #15)**

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

and

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

and

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

TvsV

TvsP

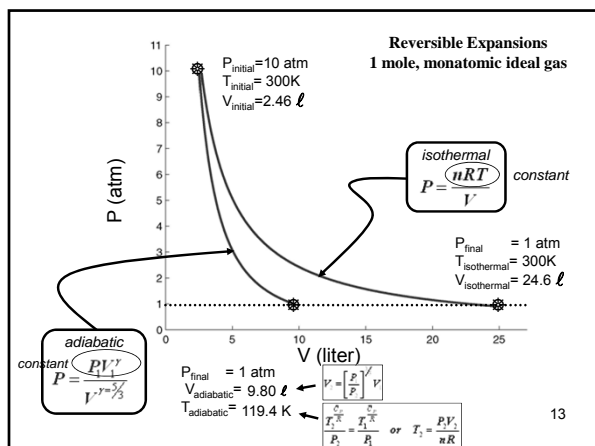
PvsV

for any two states (T<sub>1</sub>, V<sub>1</sub>, P<sub>1</sub>) and (T<sub>2</sub>, V<sub>2</sub>, P<sub>2</sub>) along an adiabatic reversible path

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

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

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

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

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{5}{3}}$$

$$T_2 = 300 \text{ K} \times (0.1)^{\frac{5}{3}} = 119.4 \text{ K}$$

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

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  $q, w$

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

vs -5.743 kJ for isothermal reversible 10 atm  $\rightarrow$  1 atm at 300K  
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**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 5 atm.

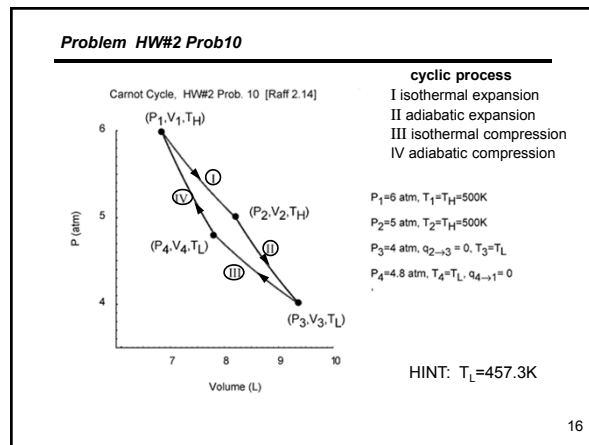
**STEP 2:** After completion of STEP 1, the gas is expanded adiabatically and reversibly until the pressure reaches 4 atm.

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

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better make it a triple

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