

# Chemistry 163B Winter 2013

## notes for lecture 5

Chemistry 163B  
Lecture 5  
Winter 2013  
Challenged Penmanship  
Notes

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First Law: ideal gas calculations

relationships that apply to **ideal gasses** for all conditions with  $w_{\text{other}}=0$  and constant composition (some also apply more generally):

$\Delta U = q + w$	$w = -\int P_{\text{ext}} dV$	$PV = nRT$
$q_V = n \int \bar{C}_V dT$ $= n \bar{C}_V \Delta T$	$q_P = n \int \bar{C}_P dT$ $= n \bar{C}_P \Delta T$	$\bar{C}_P = \bar{C}_V + R$
$H \equiv U + PV$		
<b>monatomic ideal gas</b>	$\bar{C}_V = \frac{3}{2}R$	$\bar{C}_P = \frac{5}{2}R$

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first law calculations for ideal gas no work other, constant n:

show:  $\Delta U_{\text{any conditions}} = n \bar{C}_V \Delta T$      $\Delta H_{\text{any conditions}} = n \bar{C}_P \Delta T$

$dU = n \bar{C}_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$     **general**

but  $\left(\frac{\partial U}{\partial V}\right)_T = 0$     **ideal gas**

so  $dU = n \bar{C}_V dT$   
 $\Delta U = n \bar{C}_V \Delta T$     } **ideal gas even if V or P not constant**

$H \equiv U + PV = U + nRT$   
 $\Delta H = \Delta U + nR \Delta T$   
 $\Delta H = n \bar{C}_V \Delta T + nR \Delta T$   
 $\Delta H = n(\bar{C}_V + R) \Delta T = n \bar{C}_P \Delta T$     } **ideal gas even if P or V not constant**

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isothermal reversible expansion  $P_1=10 \text{ atm} \rightarrow P_2=1 \text{ atm}$  at  $300\text{K}$

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

$\Delta U = n \bar{C}_V \Delta T$      $\Delta H = n \bar{C}_P \Delta T$   
 $\Delta U = 0$      $\Delta H = 0$

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

$w = -\int_{V_1}^{V_2} P dV = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$     } **did earlier**

$w = (1 \text{ mol}) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \ln\left(\frac{1 \text{ atm}}{10 \text{ atm}}\right)$   
 $w = -5.743 \text{ kJ}$     and     $q = 5.743 \text{ kJ}$

**NOTE:  $\Delta H \neq q$  why ???**

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First Law: ideal gas calculations

relationships that apply to **ideal gasses** for all conditions with  $w_{\text{other}}=0$  and constant composition (some also apply more generally):

$\Delta U = q + w$	$w_{PV} = -\int P_{\text{ext}} dV$	$PV = nRT$
$q_V = n \int \bar{C}_V dT$ $= n \bar{C}_V \Delta T$	$q_P = n \int \bar{C}_P dT$ $= n \bar{C}_P \Delta T$	$\bar{C}_P = \bar{C}_V + R$
$H \equiv U + PV$	$\Delta U_{\text{any conditions}} = n \bar{C}_V \Delta T$	$\Delta H_{\text{any conditions}} = n \bar{C}_P \Delta T$
<b>monatomic ideal gas</b>	$\bar{C}_V = \frac{3}{2}R$	$\bar{C}_P = \frac{5}{2}R$

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Pressure-Volume work reversible adiabatic expansion

adiabatic reversible 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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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

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ideal gas adiabatic reversible processes WORK

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

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

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

so as before ??:

$$w = - \int_{initial}^{final} \frac{nRT}{V} dV \quad \text{DUH!}$$
~~$$w = -nRT \ln \frac{V_{final}}{V_{initial}}$$~~

but T varies along path initial  $\rightarrow$  final

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

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

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

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

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

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

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

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

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

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

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

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

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

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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

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

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

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

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

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

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

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

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

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summarizing (and HW #15)

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

$$TvsV$$

and

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

$$TvsP$$

and

$$PV_1^\gamma = PV_2^\gamma \quad \text{where } \gamma = \frac{\bar{C}_p}{\bar{C}_v}$$

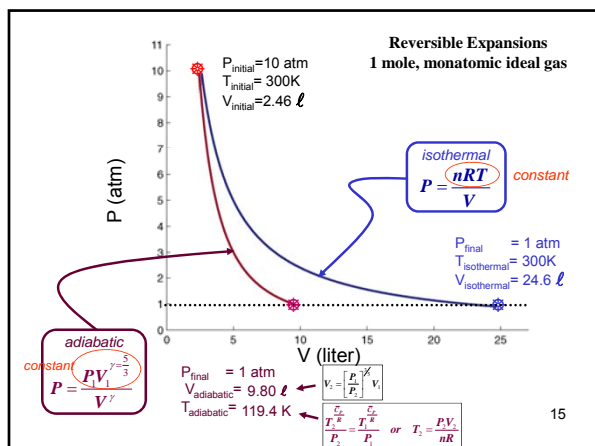
$$PvsV$$

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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## notes for lecture 5



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

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

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

$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma}{\gamma-1}}$   
 $T_2 = T_1 \left(\frac{1 \text{ atm}}{10 \text{ atm}}\right)^{\frac{5}{2}} = 300 \text{ K} \times (0.1)^{\frac{5}{2}}$   
 $T_2 = 300 \text{ K} \times (0.398) = 119.4 \text{ K}$

$\Delta T = T_{\text{final}} - T_{\text{initial}} = (119.4 - 300) \text{ K} = -180.6 \text{ K}$   
 calc  
 $\Delta U, \Delta H$   
 $\Delta U = n \bar{C}_V \Delta T = (1 \text{ mol}) (1.5) (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (-180.6 \text{ K})$   
 $\Delta U = -2.257 \text{ kJ}$   
 $\Delta H = n \bar{C}_p \Delta T = -3.762 \text{ kJ}$   
 $q = 0$   
 calc  
 $q, w$   
 $q + w = \Delta U \Rightarrow w = -2.257 \text{ kJ}$

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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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