

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):

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

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

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

$dU = n\bar{C}_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ **general**
 but $\left(\frac{\partial U}{\partial V}\right)_T = 0$ **ideal gas**
 so $dU = n\bar{C}_V dT$ } **ideal gas even if V or P not constant**
 $\Delta U = n\bar{C}_V \Delta T$ }

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

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

$V = \frac{nRT}{P}$
 $\Delta U = n\bar{C}_V \Delta T$ $\Delta H = n\bar{C}_P \Delta T$
 $\Delta U = 0$ $\Delta H = 0$

$\Delta U = 0 \Rightarrow q = -w$
 $w = -\int_{V_1}^{V_2} PdV = -nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$ $\left. \begin{array}{l} \text{did} \\ \text{earlier} \end{array} \right\}$

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

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

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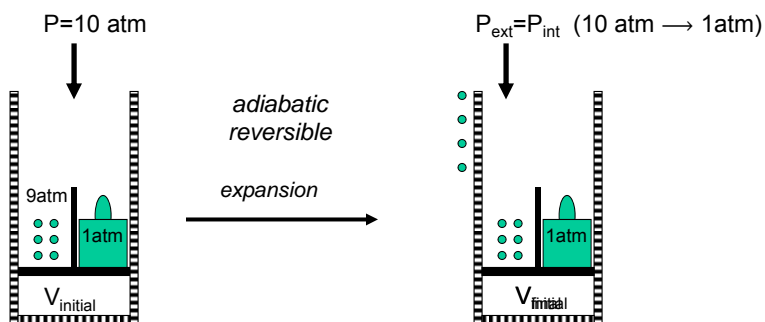
First Law: ideal gas calculations

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

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

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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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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

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

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

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

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

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

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

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

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

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

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

or

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

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for adiabatic, reversible, ideal gas: $TvsV$

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

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

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

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

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

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)

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

with

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

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

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

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

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

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

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

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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summarizing (and HW #15)

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

and

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

and

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

TvsV

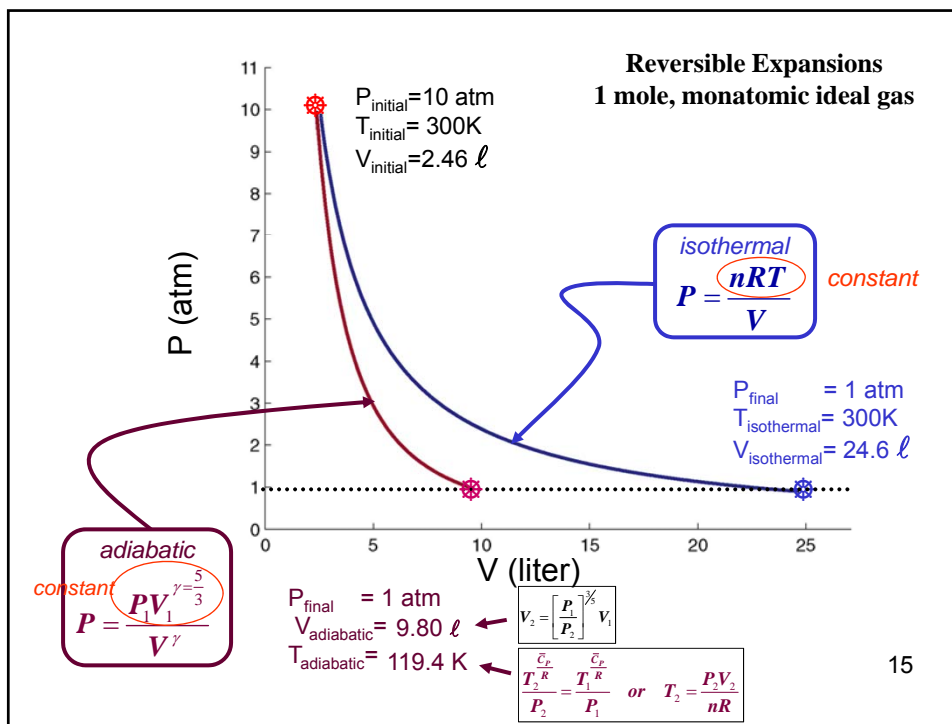
TvsP

PvsV

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

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

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

$P_2 = 1 \text{ atm}$
 $T_2 = ???$
 use T vs P

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

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

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

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

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

calc $\Delta U, \Delta H$

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

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

$$\Delta H = n \bar{C}_p \Delta T = -3.762 \text{ kJ}$$

calc q, w

$q = 0$

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

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

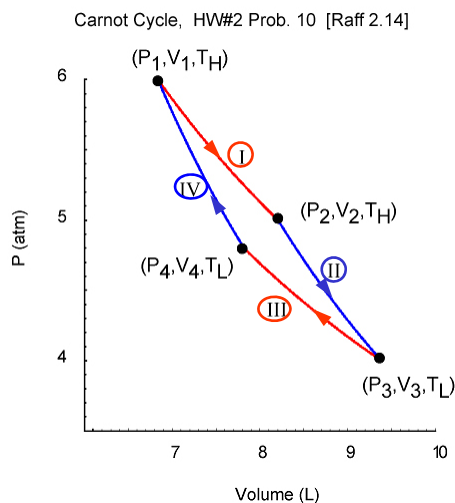
STEP 3: After STEP 2 is completed, the gas is compressed isothermally and reversibly to a final pressure of 4.800 atm.

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 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.

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Problem HW#2 Prob10



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: $T_L = 457.3 \text{ K}$

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