

Chemistry 163B Winter 2014

notes for lecture 4

Chemistry 163B
Lecture 4
Winter 2014
Challenged Penmanship
Notes

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1st Law recapitulation

U = internal energy
 $dU_{sys} = \delta q_{sys} + \delta w_{sys} + dn_{sys}$ (n =number of moles; $dn=0$ for closed system)
 $dU_{sys} = -dU_{surr}$ (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

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

- $\Delta U_{irrev} = \Delta U_{rev}$
- $\Delta V > 0, w < 0$ 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

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

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

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

- for any substance
 $dU_v = \delta q_v = n \bar{C}_v dT$ and $\Delta U_v = n \bar{C}_v \Delta T$ 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 ΔU]

- 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

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

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

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

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 → 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_{initial}, V_{initial}, T_{initial})

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

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

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

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

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

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

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

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

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 $(\frac{T_2}{T_1})^{\gamma} = (\frac{V_1}{V_2})$

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

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

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

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

for any two states (T₁, V₁, P₁) and (T₂, V₂, P₂) 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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(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

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

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

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

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

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

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

for any two states (T₁, V₁, P₁) and (T₂, V₂, P₂) along an adiabatic reversible path

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

know: T_{initial}, P_{initial}, P_{final} → calculate T_{final}

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summarizing (and HW3 #15)

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

and

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

and

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

TvsV

TvsP

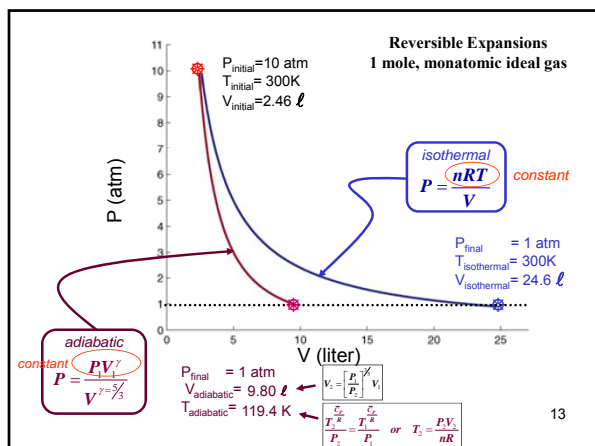
PvsV

for any two states (T₁, V₁, P₁) and (T₂, V₂, P₂) along an adiabatic reversible path

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

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

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

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

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

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.

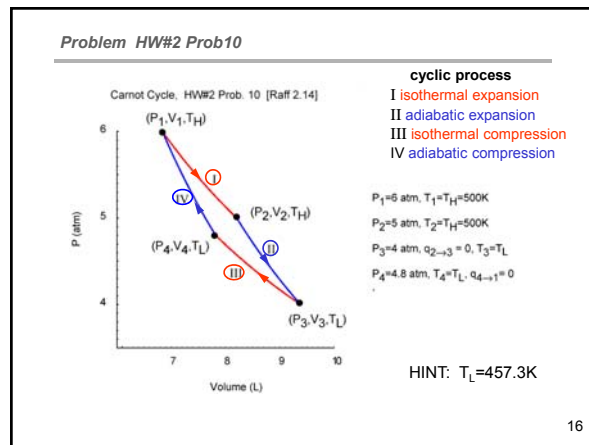
STEP 2: After completion of STEP 1, the gas is expanded adiabatically and reversibly until the pressure reaches 4 atm.

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

better make it a triple

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