# Chemistry 163B

## $q_{rev}$ , Clausius Inequality and calculating $\Delta S$ for ideal gas P,V,T changes (HW#6)

Challenged Penmanship
Notes

## *statements of the Second Law of Thermodynamics*

1. Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [*Andrews. p37]*

2. It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings. *Kelvin's Statement [Raff p 157]; Carnot Cycle*

3. It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius's Statement, refrigerator*

4. In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process
   *~ Caratheodory's statement [Andrews p. 58]*

## four steps to exactitude

**I.** $$\varepsilon_{CARNOT[ideal\ gas]} = \frac{-w_{total}}{q_U} = 1 - \frac{T_L}{T_U} = 1 + \frac{q_L}{q_U}$$

**II.** $$\varepsilon_{ANY\ REVERSIBLE\ 'TWO\ TEMPERATURE'\ MACHINE} = \varepsilon_{CARNOT[ideal\ gas]}$$

or else violation of 2nd Law

**III.** $$\oint_{cycle} \frac{đq_{rev}}{T} = 0$$ eqn 5.11 E & R; demonstrated for ideal gas Carnot;

general proof for two temperature reversible cycle;
see "a REALLY BIG RESULT" last lecture
(Dickerson p. 155; Raff p. 162 - 163)

**IV.** $$\oint_{cycle} \frac{đq_{rev}}{T} = 0$$ for any reversible cyclic process

figure 5.4 E & R
(Dickerson pp.156 - 159, Raff pp. 163 - 164)

## Entropy

$$dS = \frac{đq_{rev}}{T}$$ is an exact differential

S is a state function

## *goals of lecture*

1. Relate ΔS and $q_{irrev}$

2. Calculate ΔS for P,V, T changes of ideal gas (HW#6)
   a. using REVERSIBLE path ($q_{rev}$) ***[even for irreversible processes]***
   b. using partial derivatives of S with respect to P, V, T *[ a look ahead]*

## *entropy and heat for actual (irreversible processes): $q_{irrev}$*

an *irreversible* (actual) ***cyclic*** engine $\varepsilon_{irrev}$ coupled with a Carnot heat pump of $\varepsilon_C$ **will not** violate 2nd Law if $\varepsilon_{irrev} < \varepsilon_C$ (viz section, HO#25 SL 29;HO #28)

*$\Delta U_{cyclic}=0$*
*$-w_{total}=q_U+q_L$*
*for both rev and irrev*

***BUT** what about $q_{irrev}$ with $\varepsilon_{irrev} < \varepsilon_C$ ??*

$$\varepsilon_{irrev} = \left(\frac{-w_{total}}{q_U}\right)_{irrev} = \left(\frac{q_U + q_L}{q_U}\right)_{irrev} = 1 + \frac{(q_L)_{irrev}}{(q_U)_{irrev}} < 1 - \frac{T_L}{T_U} = \varepsilon_{reversible}$$

$$\frac{(q_L)_{irrev}}{(q_U)_{irrev}} < -\frac{T_L}{T_U}$$

$$\Delta S_{\substack{\text{cyclic engine} \\ \text{(reversible or irreversible)}}} = \frac{(q_U)_{rev}}{T_U} + \frac{(q_L)_{rev}}{T_L} = 0$$

$$\frac{(q_L)_{irrev}}{T_L} + \frac{(q_U)_{irrev}}{T_U} < 0 = \Delta S_{\text{cyclic engine (reversible or irreversible)}}$$

$$\frac{đq_{rev}}{T} = dS \qquad \frac{đq_{irrev}}{T} < dS \qquad \frac{đq}{T} \leq dS$$

# $2^{nd}$ Law of Thermodynamics in terms of entropy

- **S is a STATE FUNCTION**
- $$\Delta S = \int_{rev} \frac{đq_{rev}}{T} > \int_{irrev} \frac{đq_{irrev}}{T}$$

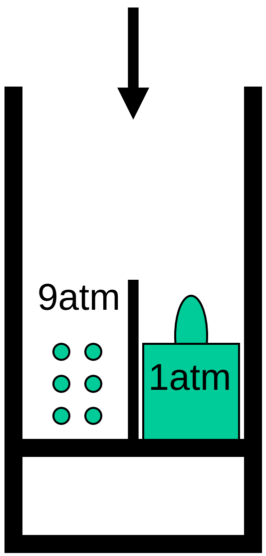
**E&R eqn 5.33 Clausius inequality**

# *Lecture 3:*
## *Pressure-Volume work   reversible isothermal expansion; $P_{ext}=P_{int}$*

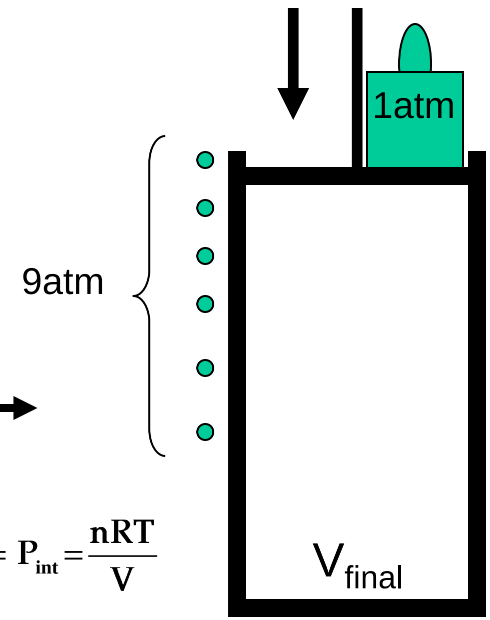
P=10 atm

isothermal

$P=P_{int}=1\rightarrow10$ atm




*expansion*




$$w=-\int_{V_{initial}}^{V_{final}} P_{ext}\,dV \qquad P_{ext}=P_{int}=\frac{nRT}{V}$$

$$w=-\int_{V_{initial}}^{V_{final}} \frac{nRT}{V}dV = -nRT\int_{V_1}^{V_2}\frac{1}{V}dV = -nRT\ln\frac{V_2}{V_1}$$

$$V_2=\frac{300K\ R\ (1mol)}{1\ atm} \qquad V_1=\frac{300K\ R\ (1mol)}{10\ atm}$$

$$w=-(300\ K\text{-}mol)\ R\ln\frac{10\ atm}{1\ atm}$$

w= -5743 J= -5.743 kJ

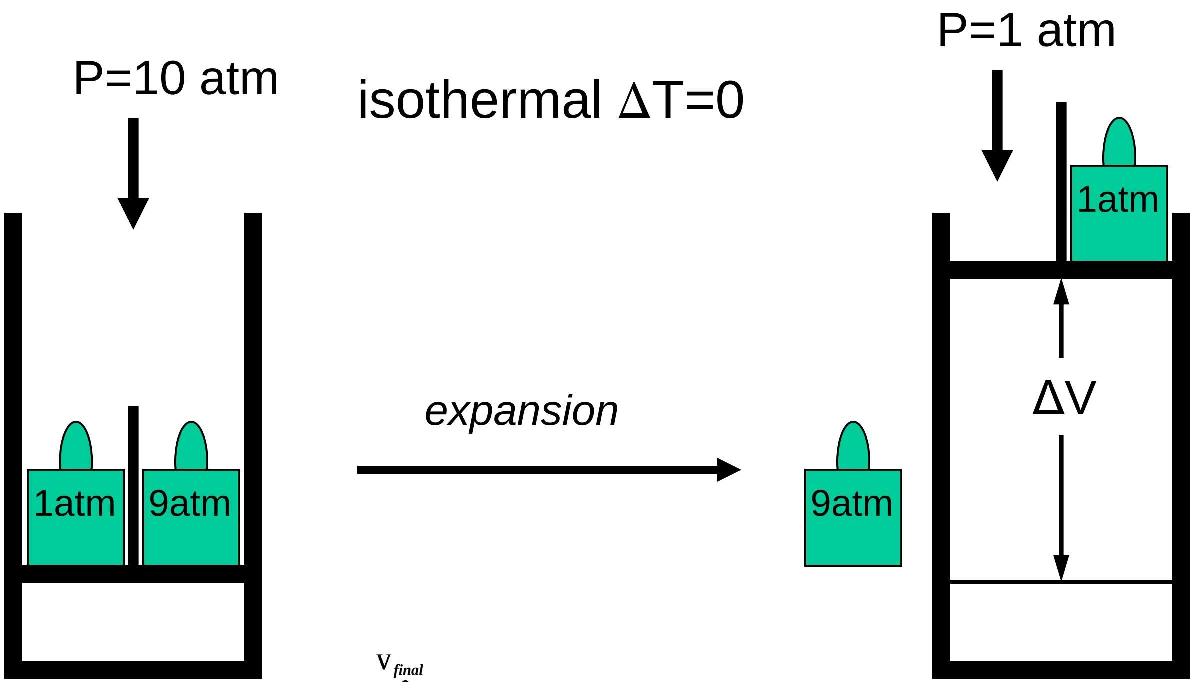
(more work done ON surroundings by reversible than irreversible; $w_{irrev}$ =-2.244 kJ)

1mole
300K
10 atm
$V_1$

1mole
300K
1 atm
$V_2$

**$q_{rev}$=-w =+5.743 kJ**

# Isothermal expansion: $P_{ext}$= const ideal gas (irreversible)




$$w = -\int_{V_{initial}}^{V_{final}} P_{ext}\, dV \qquad PV=nRT$$

1mole
300K
10 atm
$V_1$

$$w = -1\,atm\,(V_2 - V_1)$$

$$V_2 = \frac{300K\ R\ (1mol)}{1\ atm} \qquad V_1 = \frac{300K\ R\ (1mol)}{10\ atm}$$

$$w = -(300\ K\text{-}mol)\ R \left(\frac{1}{1\ atm} - \frac{1}{10\ atm}\right)$$

$$w = -2244\ J = -2.244\ kJ$$

(- sign implies net work done ON surrounding)

1mole
300K
1 atm
$V_2$

**$q_{irrev}$=-w=+2.244 kJ**

## *EXAMPLE from early lectures: isothermal expansion*

$$(P_1=10\ \text{atm},\ T_1=300\text{K},\ V_1) \rightarrow (P_2=1\ \text{atm},\ T_2=300\text{K},\ V_2)$$

initial ⟶ final

*same initial and final*

$$\int \frac{đq}{T} = \frac{q}{T} \quad \text{for isothermal process}$$

$\Delta S$

$P_{ext} = P_{int}$; $q_{rev} = 5743$ J $\quad \frac{q}{T} = 19.14\ \text{J K}^{-1}$ ?

$P_{ext} =$ const 1 atm; $q_{irrev} = 2244$ J $\quad \frac{q}{T} = 7.48\ \text{J K}^{-1}$ ?

$$\Delta S = \int_{\substack{\text{initial} \\ \text{some reversible path}}}^{\text{final}} \frac{đq_{rev}}{T}$$

to calculate Δ S must use reversible path initial → final

# $\Delta S_{universe} \geq 0$

soon :

$$\Delta S_{system} + \Delta S_{surroundings} = \Delta S_{universe} \geq 0$$

***disorder increases***

## *calculating entropy* [(see summary on review handout)]

- Thermal properties of entropy and entropy calculations
  - $dS = \frac{đq_{rev}}{T}$; $\Delta S = \int \frac{đq_{rev}}{T}$; $\oint \frac{đq_{rev}}{T} = 0$
  - $\Delta S \geq \int \frac{đq}{T}$; $0 \geq \oint \frac{đq}{T}$; $(= \textit{for reversible process}; > \textit{for spontaneous ['real'] process})$
  - $\Delta S_{total \equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
  - S is a state function; $dS$ is an exact differential
  - Dependence of S on
    - T: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
    - P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
    - V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}}$
    - Phase: $\Delta S = \frac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$
  - Calculation of entropy changes for changes in P, V, T, phase
  - Third Law and calculations using Third Law Entropies: $\bar{S}^o(T)$
  - $\Delta S^0_{reaction}(T) = \sum_i \nu_i \bar{S}^0_i(T)$
  - Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ *where* $X_i = \frac{n_i}{n_{total}}$

## look ahead - ΔS for changes in T,V; (always $\Delta S = \int_{initial}^{final} \frac{đq_{rev}}{T}$ )

**also:**

$S(T,V)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

coming very soon

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\bar{C}_v}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

**so:** $$dS = \frac{n\bar{C}_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

*always (no $w_{other}$, closed system)*

*ideal gas*

$$dS = \frac{n\bar{C}_V}{T} dT + \frac{nR}{V} dV \qquad \Delta S = \int_{rev\ const\ V\ path} \frac{n\bar{C}_V}{T} dT + \int_{rev\ const\ T\ path} \frac{nR}{V} dV$$

$$\Delta S = n\bar{C}_v \ln\left(\frac{T_{final}}{T_{initial}}\right) + nR \ln\left(\frac{V_{final}}{V_{initial}}\right)$$

*E&R eqn 5.18*

$q_{rev}$ T vary
const V path

$q_{rev}$ V vary
const T path

## look ahead- ΔS for changes in T,P; (always $\Delta S = \int_{initial}^{final} \frac{đq_{rev}}{T}$ )

**also:**

coming very soon

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{n\bar{C}_P}{T} \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$S(T,P)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

**so:** $dS = \frac{n\bar{C}_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$ *always (no $w_{other}$, closed system)*

*ideal gas*

$$dS = \frac{n\bar{C}_P}{T} dT - \frac{nR}{P} dP \qquad \Delta S = \int_{rev\ const\ P\ path} \frac{n\bar{C}_P}{T} dT - \int_{rev\ const\ T\ path} \frac{nR}{P} dP$$

$$\Delta S = n\bar{C}_P \ ln\left(\frac{T_{final}}{T_{initial}}\right) - nR \ ln\left(\frac{P_{final}}{P_{initial}}\right)$$ *E&R eqn 5.19*

$q_{rev}$ vary T
const P path

$q_{rev}$ vary P
const T path

*End of Lecture*

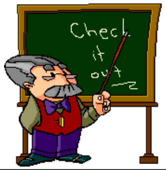
## *Return of Midterm #1*

**can't wait ?**
***pick up exam from TA in section or during office hours***

**Tianyu**
**Secs B and E**

**FRONT OF ROOM**

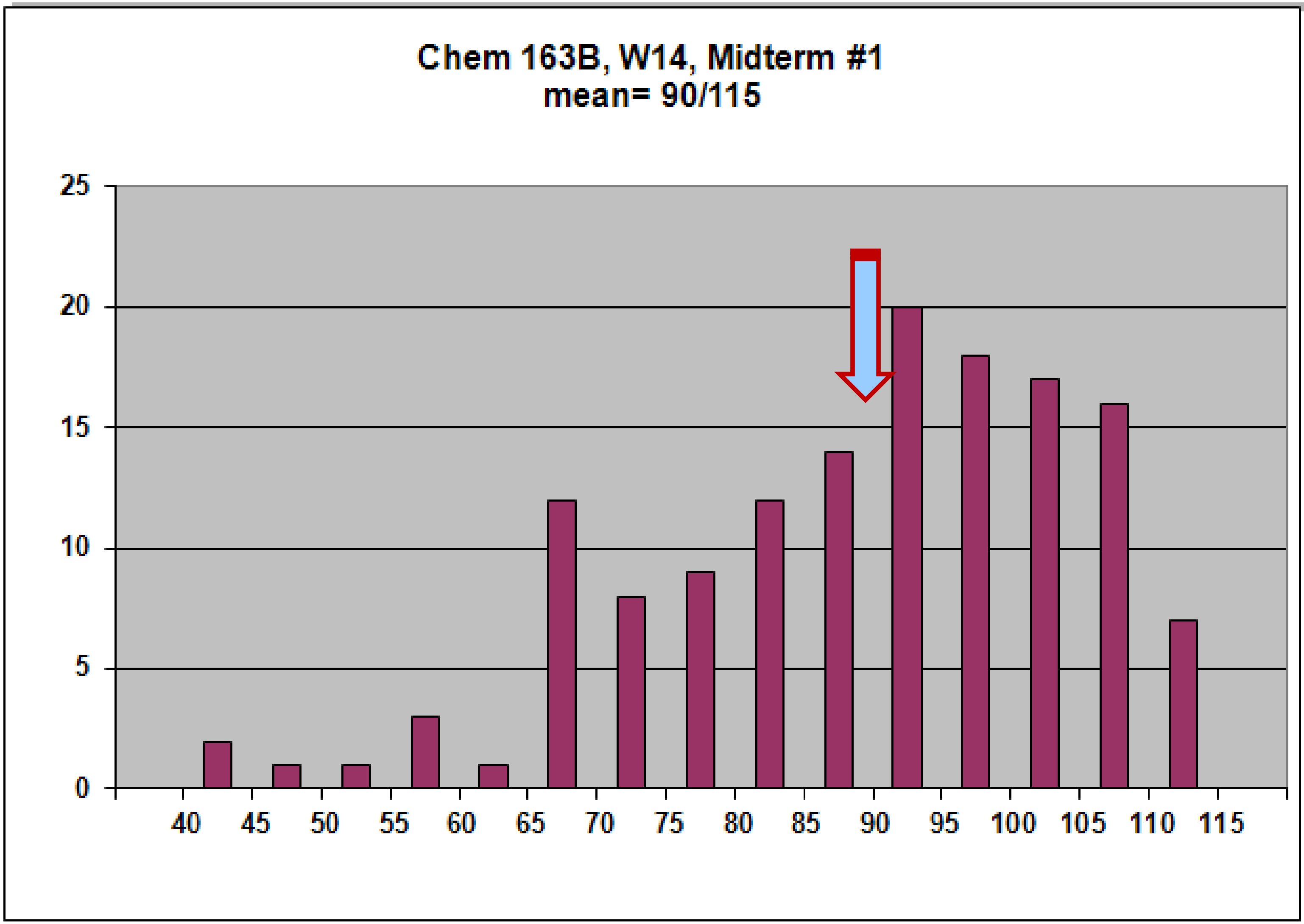
**Gabe**
**Secs A and D**



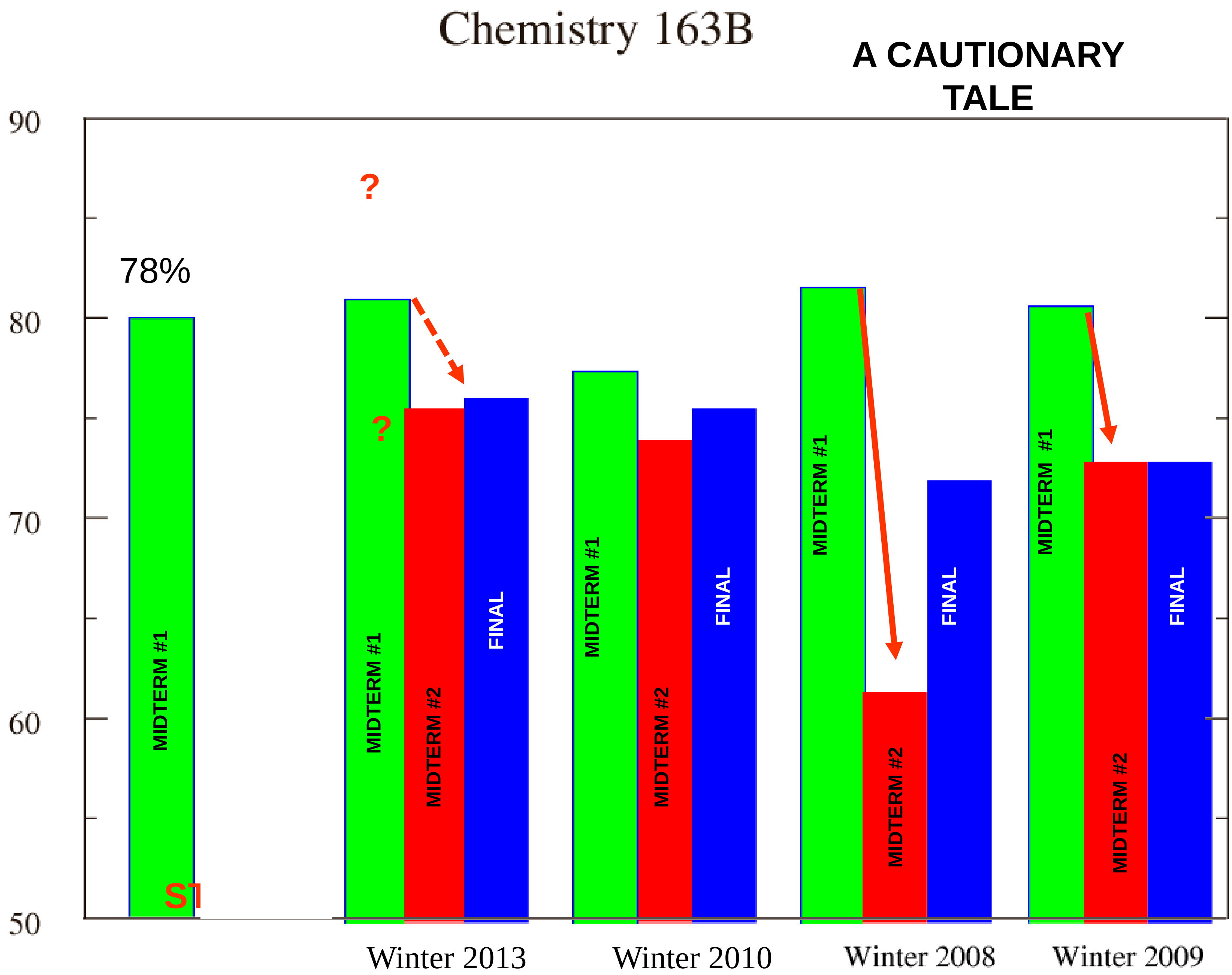
## *midterm#1 return:  the scene*

- **no grades on individual midterms (DON'T ASK !!)**
- **class continues to do well,**
  **near class average ⇨ B-**
- **TAs and Amy have keys- speak with them about any questions on exam**
- **notes on exams from E.S. ( me)**
  - ❖ **"Let me know who you are"- *props for good scores***
  - ❖ **"Need to do better"- *I'm happy to meet with you***
  - ❖ **"     "- can always do better, and we do care about you too !!**

# *Midterm #1 Winter 2014*




• total pts for qtr (115 + 138 + 162 + 46) = 115+ 347 = 464


Chemistry 163B
A CAUTIONARY TALE
90
80
70
60
50
78%
?
?
S1
MIDTERM #1
MIDTERM #2
FINAL
Winter 2013
Winter 2010
Winter 2008
Winter 2009

## *Return of Midterm #1*

**can't wait ?**

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**Tianyu**
**Secs B and E**

**FRONT OF ROOM**

**Gabe**
**Secs A and D**