CHEM 206 section 01

LECTURE #2 Wed. Jan. 09, 2008

ASSIGNED READINGS:

TODAY'S CLASS: continue Ch.6 (& 9.10)…

NEXT CLASS: finish Ch.6
start Ch. 19.1-19.5

Remember: ***labs/tutorials start this week***
Chem 101 seminars this & next week

(1)

6.4 The First Law of Thermodynamics

1st Law: The energy of the universe is constant.

"ENERGY BOOKKEEPING": 1st law in mathematical form

If a system loses energy (as either HEAT or WORK),
the energy must go into the surroundings… & vice versa

$$\Delta E = q + w$$

ΔE = change in system's "internal" energy
q = heat (heat leaving system = -ve)
w = work (work done by system = -ve)

Internal Energy "E" = sum of all potential and kinetic energies of the atoms, molecules or ions in the system…

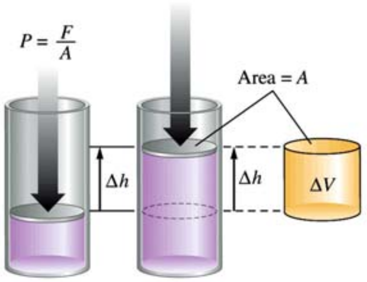
…hard to determine, but measuring CHANGES (ΔE) is easy

(2)

What is work? See: Kotz p.252 *A Closer Look* at bicycle pumps

Work is energy spent PUSHING matter around.
…happens if a system's VOLUME changes!

- **Important for gases ⇨ easy to expand or compress!**
- **NOT important if only solids & liquids are involved**



$V_{cylinder}$ = $Area_{base}$ × height
$\Delta V = (\pi r^2) \times \Delta h$

Work = force × distance

and: Pressure = $\frac{\text{force}}{\text{area}}$

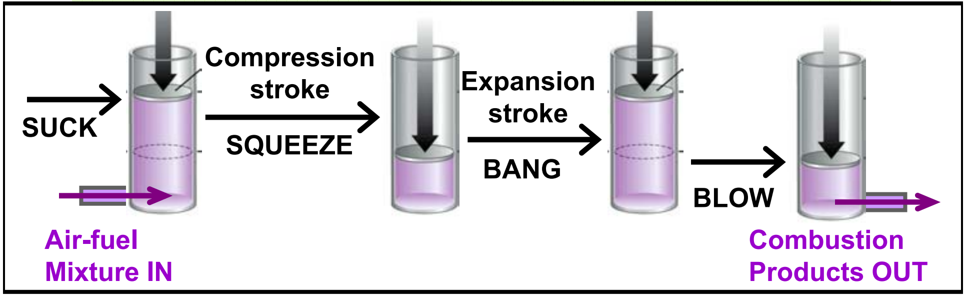
$$\Rightarrow \text{Work} = \text{pressure} \times \underbrace{\text{area} \times \text{distance}}$$

⇨ *"PV work"* $w_{system} = -P\,\Delta V$

SIGN CONVENTION:
Expanding gas ($\Delta V > 0$)

- pushes up piston ⇨ performs work
- system loses some E ⇨ negative

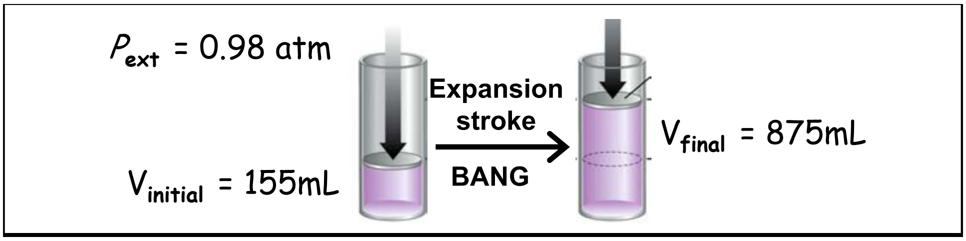
Controlled explosions: PV work in an engine



When the spark ignites the fuel-air mixture inside a cylinder in a standard 4-stroke automobile engine, the resulting gaseous combustion products expand against a constant external pressure P_{ext} of 0.98 atm (*i.e.*, atmospheric P).

IF: Volume at end of compression stroke = 155 mL
Final volume after expansion = 875 mL,

what quantity of work is done during the expansion stroke?



$w = -P_{ext}\,\Delta V$

$= -(0.98\ \text{atm})(0.875 - 0.155\ \text{L})$

$= -0.706\ \text{L·atm}$ ⇨ $= -0.71\ \text{L·atm}$ *(2 SF)* → *in a strange E unit !*

⇨ NEGATIVE WORK MEANS WORK DONE BY SYSTEM

NOTE: use gas constant to derive conversion factor to Joules
$R = 0.08206\ \text{L·atm·mol}^{-1}\text{K}^{-1} = 8.314\ \text{J·mol}^{-1}\text{K}^{-1}$

THUS: $w = -(0.706\ \text{L·atm})(101.3\ \text{J·L}^{-1}\text{·atm}^{-1})$

$= -71.52\ \text{J}$

⇨ $= -72\ \text{J}$ *(2 SF)*

Different types of energy functions (Kotz 6.5)

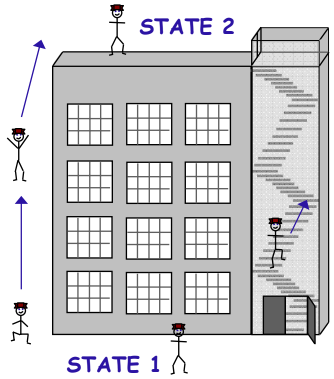
State functions *vs.* Path functions

Quantities that describe present state of system
- ***path-independent***
- *i.e.,* does not matter how system arrived in that state

e.g., internal E
potential E
kinetic E
& others…

Quantities of energy that **depend on path taken** to change between two states

e.g., heat
work…



6.5

For processes occurring at constant pressure, heat flow (q_p) reveals a change in bond strengths

EXOTHERMIC:

- *Heat E leaves system: $q_p < 0$*
- the new bonds formed are stronger overall (more stable) than the bonds broken
- due to bond type and/or #

Example: $\Delta H_{rxn} < 0$

ENDOTHERMIC:

- *Heat E enters system: $q_p > 0$*
- the new bonds formed are weaker overall (less stable) than the bonds broken
- due to bond type and/or #

Example: $\Delta H_{rxn} > 0$

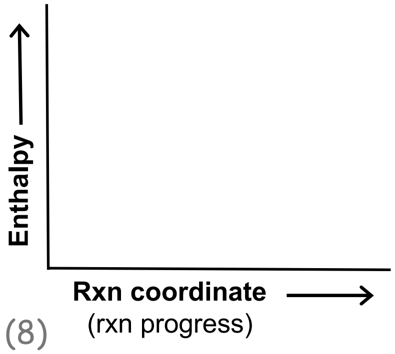
HEAT OF REACTION: ΔH_{rxn} = enthalpy change for rxn

= difference in chemical potential E of products & reactants
= difference in "**ENTHALPY**" **(H)**

Using a thermochemical equation to understand a rxn

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H^o_{rxn} = -890$ kJ
(per mole CH_4 reacted)

1. What can we say about the bonding in reactants *vs.* products?
2. Complete the reaction coordinate diagram below.
3. How much heat is evolved when 28 L of methane gas (CH_4) is burned in air (*i.e.,* excess oxygen)?



ANS ⇨ EVOLVES 1100 kJ of heat

Enthalpy (H): a state function related to bond strengths

Chemical potential E = stabilization due to BONDS
Stronger bond ⇨ more stabilization
⇨ more heat released when bond FORMS
⇨ more heat required for bond to BREAK

ΔH_{rxn} = Difference in chemical pot'l E between products & reactants
= net E difference due to some bonds broken & new ones formed
= HEAT FLOW FOR RXN/PROCESS AT CONSTANT PRESSURE

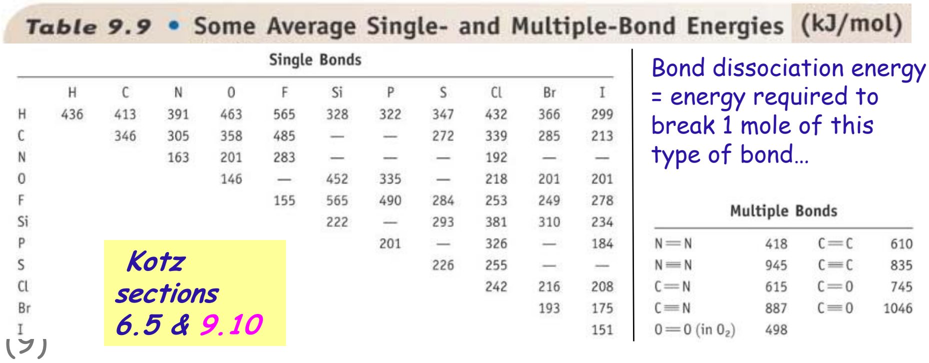


Table 9.9 • Some Average Single- and Multiple-Bond Energies (kJ/mol)

Single Bonds

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	413	391	463	565	328	322	347	432	366	299
C		346	305	358	485	—	—	272	339	285	213
N			163	201	283	—	—	—	192	—	—
O				146	—	452	335	—	218	201	201
F					155	565	490	284	253	249	278
Si						222	—	293	381	310	234
P							201	—	326	—	184
S								226	255	—	—
Cl									242	216	208
Br										193	175
I											151

Bond dissociation energy = energy required to break 1 mole of this type of bond…

Multiple Bonds

N═N	418	C═C	610
N≡N	945	C≡C	835
C═N	615	C═O	745
C≡N	887	C≡O	1046
O═O (in O_2)	498		

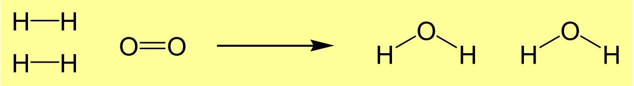
Kotz sections 6.5 & 9.10

EXAMPLE: Use bond energies to estimate ΔH_{rxn} for the formation of water from the elements (& then compare to experiment…):

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ By expt: ΔH_{rxn} = -285.83 kJ/mol H_2O

Based on bonds broken *vs.* bonds formed, we can estimate the enthalpy difference between "state 1" = reactants *AND* "state 2" = products:

BDE data:
H-H 436 kJ/mol
O=O 498 kJ/mol
O-H 463 kJ/mol



Bonds broken:
(ENERGY INPUT)
1 H-H bond per H_2: 2 ~~mol~~ x 436 kJ·~~mol^{-1}~~
1 O=O bond per O_2: 1 ~~mol~~ x 498 kJ·~~mol^{-1}~~
+1370 kJ

Bonds formed:
(ENERGY OUTPUT)
2 O-H bonds per H_2O:
4 ~~mol~~ x 463 kJ·~~mol^{-1}~~
−1852 kJ

Input + Output = $\Delta H_{rxn} \approx \Sigma BDE_{bonds\_broken} - \Sigma BDE_{bonds\_formed}$

So: $\Delta H_{rxn} \approx$ -482 kJ (exothermic) for 2 mol H_2O ≈ **-241 kJ/mol H_2O**

Close, but not exact match to experiment because:
- BDEs valid for isolated, gas-phase molecules…
- in rxn, molecules clearly NOT isolated ⇨ interaction E involved…

6.6 Calorimetry: measuring heat flow in the lab

From 1st law: $\Delta E = \underbrace{\Delta H}_{\text{HEAT}} - \underbrace{P\Delta V}_{\text{PV WORK}}$

Does our exp'tal apparatus allow PV work, or not?

CALORIMETER = apparatus for measuring heat flow in/out of an object, reaction, physical process…

Two basic types of calorimeters:

1. Constant pressure calorimeter (open to atmosphere)
2. Constant volume calorimeter (sealed vessel)

Is pressure constant?
- *e.g.,* open to air
- system's volume is allowed to change freely

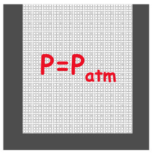
yes → **Heat flow = q_p = ΔH**

no → **Heat flow may include extra E…** …if # moles gas changes, but system not allowed to expand or contract!

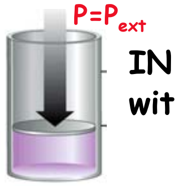
Set-up #1: system at constant pressure = P_{ext}

VOLUME OF SYSTEM CAN CHANGE IF IT NEEDS TO…

OPEN VESSEL



or



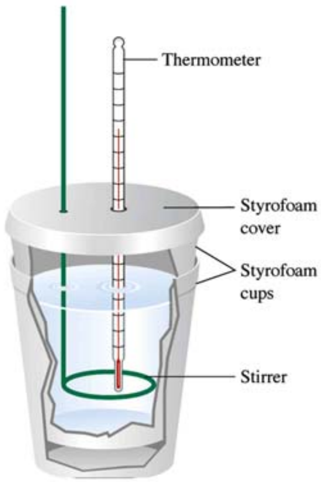
IN CYLINDER with const-P piston…

From 1st law: $\Delta E = \underbrace{q}_{\text{HEAT}} - \underbrace{P\Delta V}_{\text{PV WORK}}$

If process involves…	**Does volume change?**	**Work done?**	**Measuring heat flow (q_p) tells us…**
Change in # moles of gas	Expands or contracts…	Yes	$q_p = \Delta H$ & total $\Delta E = \Delta H - P\Delta V$
Only solids or liquids	Not really	No	$q_p = \Delta H$ & $\Delta E = \Delta H$ *since w=0* *Here, all E change is due to heat.*

Constant pressure calorimetry

Use this in Expt.#2



See Figure 6.16:
A "coffee-cup calorimeter"

Const. P ⇨ $q_{rxn} = \Delta H_{rxn}$

Heat released by reaction is absorbed by (solution & calorimeter)…

$$0 = q_{rxn} + (q_{soln} + q_{calorimeter})$$
$$-q_{rxn} = q_{soln} + q_{calorimeter}$$

Calibrate 1st to find its "C"

(13)

Think about the following reactions…
(performed under constant pressure conditions)

1.) $Mg(s) + 2HCl(aq) \rightarrow H_2(g) + MgCl_2(aq)$

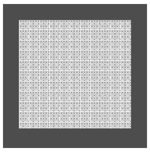
2.) $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

3.) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Rxn	Δn_{gases}	Any work?	Sign of ΔV	Sign of work	ΔH *vs.* ΔE *Equal or not?*
1					
2					
3					

On your own: consider rxn 1 with 1 mole of Mg (as limiting reactant) & calculate the work done (P_{ext} = 1 atm, T = 298 K)

Set-up #2: sealed, constant-volume container



Sealed vessel, called a bomb

VOLUME OF SYSTEM CANNOT CHANGE.

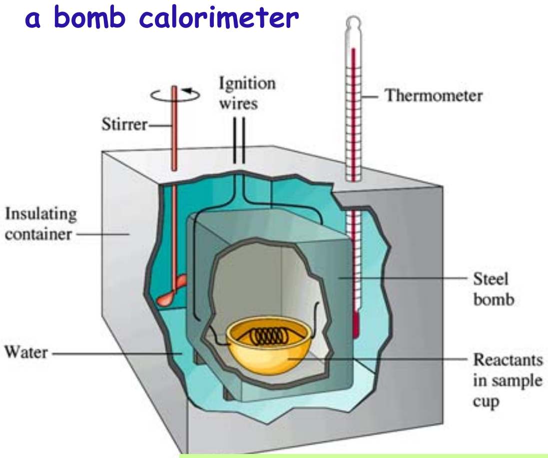
THUS: PRESSURE MIGHT BUILD UP (extra E "trapped") **or DROP** (less E…)

From 1st law: $\Delta E = \underbrace{q}_{\text{HEAT}} - \underbrace{P\Delta V}_{\text{PV WORK}}$

If process involves…	**Volume changes?**	**Work done?**	**Measuring heat flow (q_v) tells us…**
Net gas formation $\Delta n_{gases} > 0$	No - it can't!	No!	$\Delta E = q_v - 0$ ⇨ Learn nothing of ΔH. Energy normally spent by expanding is trapped as heat…not just ΔH's heat.
Net gas consumption $\Delta n_{gases} < 0$	No - it can't!	No!	$\Delta E = q_v - 0$ ⇨ Learn nothing of ΔH. No energy gained by surr. compressing system… ∴ less heat than system's bond rearrangements should yield.

Constant volume calorimetry

See Figure 6.17:
a bomb calorimeter



Heat capacity of whole calorimeter known in advance…

$$q_{calorimeter} = -q_{rxn} \text{ (}\underline{\text{not}}\ q_p\text{)} = -\Delta E_{rxn}$$

Because $\Delta E_{rxn} = q + w$
& no E lost as work here…

This is how calorie content of food is determined…
→ Find ΔE_{rxn} for combustion (similar rxn to metabolism)

ASSIGNED READINGS:

BEFORE NEXT CLASS: **Review and…**

***Read 206 material:** Ch.6 sections 6.1-6.6 & 9.10

\+ WORK ON Ch.6 PROBLEMS (up to #42)

BEFORE FIRST LAB:

***Review from 205:** Ch.12 concepts, & read 12.6-12.9

Remember:

- Labs start THIS WEEK (Tues aft, Wed aft, Thurs eve.)
  arrive prepared: lab coat & glasses
  completed Expt.#1 prelab
  completed tutorial homework
- Chem101 seminars this Friday & next week